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[FOURTH SERIES.]

ART. XX.—*The Transition Temperature of Sodic Sulphate, a New Fixed Point in Thermometry;* by THEODORE WILLIAM RICHARDS.

I. *On the Constancy of the Point in Question.*

With the assistance of JESSE BRIGGS CHURCHILL.

ACCORDING to the Phase Rule of Willard Gibbs, in order to obtain a nonvariant point in any system two more conditions must be definitely fixed than the number of components in the system. In other words, if the system contains only one component, three conditions must be fixed; if two components, four conditions, and so on. Since such a nonvariant* point is invariable in temperature, as well as in every other respect, there evidently exist a great number of definite temperatures obtainable by the combinations of different substances.

Of these multitudinous nonvariant points, the world uses only two, the simplest possible, as the standards of thermometry. The fixed conditions are:—a definite pressure, and two phases of one component, water. While undoubtedly 0° and 100° Centigrade will always remain the standards of reference, it would be extremely convenient to have at least one definitely determined point between these. Many thermometers do not cover this whole range, and all are noticeably upset as to their internal condition by such wide variations of temperature.

Landolt's very carefully made determinations of the melting

*Trevor's term "nonvariant" is a peculiarly happy selection. His similar terms "monovariant," etc, would be equally suitable if they were not hybrids of Greek and Latin. Would it not be well to use instead of these the homogenous words "univariant," "bivariant," etc? These latter terms are not likely to cause trouble because of their similarity to "univalent," etc, for both the numbers of syllables and the accents are different in the two series.

points of a number of organic substances* showed that these bodies are too much subject to contamination with clinging impurities to serve as accurate standards. Organic compounds are too plentiful in number to make the easy obtaining of any one alone an easy matter, and among inorganic substances no single suitable substance beside water seems to exist.

There is no reason, however, why we should be confined to the use of a single component in this search for fixed points. Two components, requiring four fixed conditions, should answer equally well. The only essential is that the substance involved should form perfectly definite phases, and should be capable of being obtained in the pure state. Nernst has suggested the use of "cryohydric" points as a means of maintaining constant low temperatures, but the possibility of utilizing higher nonvariant points involving two components as a basis of thermometry and a means of maintaining constant temperature does not seem to have been generally realized.

Of the many pairs of substances which might serve the purpose in view, the pair, sodic sulphate and water, seems to be the most suitable for several reasons.

In the first place, the system (Na_2SO_4. + $Na_2SO_4.10H_2O$ + saturated solution + vapor) is in equilibrium at 32·5°†—a most convenient point, less above ordinary temperatures than 0° is below them, and within the field of even very large-bulbed thermometers. This small elevation involves very little disturbance in the tension of the glass, as well as very slight correction on account of the column projecting into the cooler atmosphere of the room. Moreover 32·5° is near the temperature of greatest difference between the hydrogen and the mercury thermometer.

On the other hand, sodic sulphate does not "melt" so easily as to cause any difficulty in keeping it unfused in a reasonably warm place. A substance melting only a few degrees lower would be continually freezing into a solid lump, which could be extracted from its bottle only by melting. The fact that it is not deliquescent is also of value.

A much more important advantage, as far as exactness is concerned, is to be found in the great ease with which the substance may be obtained in a pure state. Its solubility is far less at 10° than it is at 33°, hence its recrystallization by cooling does not involve much loss. Moreover, it may also be crystallized in the anhydrous state by simply melting the aqueous crystals, and since this process necessarily brings into play a wholly new set of isomorphous relations, it may be relied upon to eliminate impurities which are not rejected by the hydrated crystals.

* Zeitschr. phys. Chem., iv, 349 (1889).

† Lowenherz found 32·39° (Zeitschr. phys. Chem., xviii, 70).

Again, the "melting" absorbs enough heat to insure the rendering "latent" of any heat evolved by the mechanical process of gentle agitation, or of any heat taken in from the environment. The semi-opaque nature of the mixture removes any serious danger from radiant heat.

Since the volume scarcely changes with the transition, reasonable alterations in pressure do not cause any essential change in the temperature. This fact may be of importance if one has occasion to use very deep layers of the mixture.

The number of possible hydrates is smaller in this case than in many, hence the change is a sharp one. The salt $Na_2SO_4.7H_2O$ is so soluble that it cannot exist in the presence of either of the other solid phases.*

Last, but not least, Glauber's salt is extremely inexpensive, and at hand in every chemical and physical laboratory. Oddly enough, the melting point of the anhydrous salt, 865°, is one of the most satisfactory standards among high nonvariant temperatures.

It is needless to state that the usual precautions necessary to obtain accurate results were taken in the thermometric work which follows, as well as in the chemical preparation. Several thermometers were used in the course of the experiments; they will be described as the account progresses. For the first determinations, which were wholly of a relative nature, a Beckmann thermometer of the first quality, made by Goetze of Leipzig, was chosen. This instrument was graduated to hundredths of a degree, and could be easily read to within a thousandth. Because of the thinness of its bulb, this thermometer was especially sensitive to pressure; hence it was guarded carefully during its use. It was always read in a vertical position, as were all the other thermometers. Since the temperature of the room remained essentially constant during the preliminary experiments, the barometric pressure did not change by important amounts, and the height of the mixture around the bulb was always about the same, the readings are directly comparable with one another without correction.

First Problem—The effect of the Temperature of the Environment.

At first sodic sulphate prepared by crystallizing twice in a porcelain dish the ordinary "purissimum" material of commerce was used. This preparation was coarsely powdered and

*The non-existence of the substance $Na_2SO_4.H_2O$ may now be considered proved. Even if it really exists, however, the facts recorded below remain; one must merely read "monohydrated" instead of "anhydrous," and the theory will be unchanged. See de Coppet, Berichte d. d. Ch. Gesell., xii, 248; also, Lescoeur, Ann. Chim. Phys. [6], xxi, 526 (1890).

partly dried in a desiccator. When placed in a wide test-tube surrounded by a Beckmann air-jacket (a still wider test-tube) and allowed to remain for an hour in a thermostat at 32·9°, it melted with absolute constancy at a temperature indicated on the arbitrary scale by 4·758. On the following day, upon being replaced in the thermostat the "melting" point appeared to be precisely the same. It was found advantageous to melt the crystals partially into a pasty mass, by means of a gas-lamp, before immersing them in the thermostat, and the mass was stirred gently by a ring-shaped platinum stirrer. Upon raising the temperature of the bath to 36° not the least change was observed, although this application of a higher temperature was allowed to continue for half an hour. A lower temperature, on the other hand, had a less satisfactory effect. When the bath was kept at 29° the thermometer in the sodic sulphate indicated a constant reading of 4·746, a depression of 0·012°. In order to verify this phenomenon, a purer specimen, which melted at 4·760° with the bath about 33°, was surrounded by an environment at 30°, and then indicated 4·750° on the arbitrary scale.

Thus it is evident that the most satisfactory results are to be obtained by melting the salt slowly, and not by allowing it to solidify. The reason for this is obvious. The anhydrous salt is far less apt to form supersaturated solutions than the hydrated salt, and the crystals instantly melt upon being heated above their transition point, absorbing an appreciable amount of heat in the process. On the other hand, in order that the mass may solidify, the anhydrous salt must dissolve while the supersaturated solution is depositing its hydrate, both of these operations being much less prompt than the preceding. In all subsequent determinations the thermostat was kept about half a degree above the point sought, and it was found that the mixture would then melt so slowly as to last for hours.

Second Problem—Concerning the Purity of the Salt Required.

Löwenherz* has found, under van't Hoff's direction, that an admixture of foreign substances lowers the transition temperature of sodic sulphate just as it does simpler melting points. Hence a study of the purification of the salt is of great importance for our present purpose.

The mother-substance used in preparing the salt above was found to melt at a temperature of 0·06° below that which had been twice recrystallized in porcelain. Four further crystallizations in platinum vessels changed the transition temperature only 0·002° above that corresponding to two recrystallizations, the arbitrary scale indicating 4·760°.

* Loc. cit.

While it seemed probable that this recrystallization had freed the salt from anything which could affect its melting point, further proof seemed proper. Hence a kilogram or so of pure sodic hydric carbonate was thoroughly washed with pure water, and was then dissolved in an excess of pure dilute sulphuric acid. After six crystallizations the salt was still perceptibly acid to methyl orange, and hence after testing the melting point the salt was recrystallized again, collected on a large Gooch crucible and washed. Although now free from any trace of acid, it was precipitated as anhydrous salt by heating to 100° (the mother liquor being rejected), redissolved at 33°, and recrystallized by cooling. These final operations were conducted with the purest water and all the precautions necessary in the most refined work. A portion of the later mother liquors was neutralized with pure soda and twice recrystallized in order to obtain a third sample.

Another thermometer was used in testing the melting points of these three samples. This thermometer, admirably made by Baudin of Paris in 1880, is graduated to the fiftieth part of a degree, and can be read by means of a telescope and micrometer to within a thousandth. Its scale is about forty centimeters long, and covering the twelve degrees between 21° and 33°, including the zero point below a small auxiliary bulb. This small bulb was always in the thermostat, leaving only about 10° of the column to be corrected for the lower temperature of the room. Following are the uncorrected results obtained with this thermometer:

The slightly acid salt melted at	**32·520**
The neutralized and recrystallized salt melted at	**32·560**
The purest, nine times recrystallized salt melted at	**32·561**
The twice recrystallized salt first made melted at	**32·560**

The last observation was made in order to compare this series with the other which has been made with the Beckmann thermometer. As the pressure had increased since the other readings were taken, the arbitrary thermometer itself could not be satisfactorily compared with that of French manufacture.

Evidently it is a matter of no great difficulty to obtain sodic sulphate of constant "melting point." Even two recrystallizations of the purest Glauber's salt of commerce carried on in porcelain vessels seemed to be enough to eliminate any serious impurity. In order to obtain certain results, the purification should be continued until the melting point is constant. The repeated recrystallization of the slightly acidified salt is especially instructive in this regard, for it is safe to conclude that when the acid has gone other accidental impurities would have disappeared also; and the methyl orange test is one of extreme delicacy if the solution is not too concentrated.

Third Problem—The Effect of Varying the Mass of the Phases.

Theoretically, of course, a change in the relative amount of the phases should cause no difference in the nonvariance of the point under consideration provided that no one phase totally disappears. But since the superficial area of either solid present is a factor in determining the speed of the adjustment of the equilibrium, it was thought that varying proportions might cause a slightly varying "temperature lag." Nevertheless, as a matter of fact, no reasonable increase in the amount of either of the solids or of the liquid seemed to cause the least effect, provided that the process was one of melting and not of solidifying, and the mixture was properly stirred. The Beckmann thermometer remained always at 4·760 as long as the barometer stood near to the normal height. In order to insure the rapid establishment of the equilibrium it was our custom to have always some anhydrous powder present in the first place. This precaution also renders harmless drops of water introduced on the washed thermometer or the stirrer. It is well to powder also the hydrated salt, or at least to use it in the form of fine crystals, so as to increase its surface.

Since the point in question seems then to fulfil all the requirements of an accurate standard of reference, manifestly its relations to the international standard should be established.

II. *Reference to the International Standard.*

The only good thermometers indicating 33° at hand in the chemical laboratory are two of a set (one of which has already been mentioned) made by Baudin, and these have not been accurately calibrated. On one occasion thermometer Baudin No. 9,389 indicated 32·570° as the point in question, and immediately afterward came to 0·097° in pure melting ice, a difference of 32·473°. Subsequently the same thermometer indicated a change of 32·560−0·086=32·474; while the other thermometer (No. 9,390) gave on two successive trials separated by perhaps a week 32·560−0·084=32·476 and 32·550−0·083=32·467. The mean of all these values is 32·472, and to this about 0·009* must be added to correct for the column of 10° exposed to the temperature of the room (about 26°). No other corrections are possible, and there is no further guarantee of the accuracy of the number 32·481° than the evident care used in the construction of the thermometers and the fact that they agree very closely. It is probable that the instruments were made to be used vertically, hence no correction to the horizontal position is needed.

* See tables by Rimbach in Landolt und Börnstein, page 143.

In order to decide more definitely the exact value, Professor Sabine was so kind as to bring from the Jefferson Physical Laboratory of Harvard University two of the admirable standards in use at that institution. These two instruments, the thermometers Nos. 11,142 and 11,143, of Tonnelot, have been subject to extremely minute scrutiny and calibration. They are of course accompanied by a very detailed report from the Bureau Internationale des Poids et des Mesures, and upon this are based all the corrections recorded below, except the last. This one, necessitated by the fact that the thermometers were not wholly immersed in the constant mixture, was calculated from the relative cubic expansion of glass and mercury. The length of the column exposed to the temperature of the room (25·5°) was estimated carefully with the help of another thermometer, and was found to be about 22° allowing for the conductivity of the glass and mercury. The correction, 0·024°, agrees closely with Rimbach's* empirical values, although his were not intended for such small corrections; probably it is not more than 0·003° in error.

Both thermometers are about six decimeters long, and have their hundred degrees divided into tenths. With the help of the accurate Geneva cathetometer employed, they could probably be read to within $\frac{1}{5\,0\,0}$°. The readings were made with the coöperation of Professor W. C. Sabine.

THE TRANSITION TEMPERATURE OF SODIC SULPHATE.

	Thermometer 11,142 Tonnelot.	Thermometer 11,143 Tonnelot.
Reading at transition point	+32·400	+32·498
Reading in melting ice	+ 0·120	+ 0·101
Uncorrected difference	+32·280	+32·397
Correction for calibration	+ 0·147	+ 0·028
" " interior press. (32°)	+ 0·0330	+ 0·0328
" " " " (0°)	− 0·0076	− 0·0075
" " exterior press. (32°)	− 0·0006	− 0·0006
" " " " (0°)	+ 0·0007	+ 0·0007
" size of divisions	+ 0·0104	+ 0·0059
" for projecting column	+ 0·024	+ 0·024
Transition point according to mean Parisian mercury thermometer	+32·487	+32·480

The purest sodic sulphate, and ice from water which had just been twice distilled in platinum (from permanganate, and then from a trace of acid potassic sulphate) were used, and the usual precautions of all kinds were taken. The readings were made with the thermometers vertical: they are reduced to the horizontal position above. The corrected barometer stood at 761^{mm} during the higher readings, and at 762·5 when the ther-

* Rimbach, loc. cit.

mometers were in ice. The middles of the bulbs were about 45^{mm} below the surface of the inverting mixture and about 37^{mm} under the ice water. The pressures corresponding are about $4{\cdot}5^{mm}$ and $5{\cdot}7^{mm}$ of mercury respectively. The sum total of the corrections for exterior pressure is wholly insignificant; they are included above only for the sake of completeness. One division of No. 11,142 equals 1·000320 standard mercury degrees, while one of No. 11,143 equals 1·000181 degrees.

The two results (32·487° and 32·480°) are probably as nearly equal as could be expected, considering that three of the four readings unfortunately fell on dividing lines.

The agreement of the average 32·484 with the result 32·481 obtained from Baudin's uncorrected instruments is notable; evidently the empirical graduation of the older day included a close approximation to most of the corrections. The result of Löwenherz, 32·39°, is the only previous value with which it is worth while to compare this, but his was meant only for relative work and was referred merely to "a normal thermometer" of uncertain origin.

While it would be unsafe to predict the precise limit of error of the final value 32·484 (or 32·379 referred to the hydrogen thermometer) the result is certainly near enough to the truth to be a great boon to those who have not a standard instrument at their disposal. If, as is usually the case, it is only desired to attain a result accurate to within $\frac{1}{100}$ degree, the thermostat is unnecessary. Surprisingly accurate results may be obtained in the ordinary Beckmann freezing-point apparatus, if the outer bath is a degree or two above the point desired.* In fact, it is really an easier point to use than either of the old points, for one can keep neither ice nor steam always at hand in a bottle. Probably the inversion temperature might be of great use as a means of maintaining large vessels at a perfectly constant temperature: this point deserves consideration. Moreover, while sodic sulphate has several advantages as a standard, there are undoubtedly many other substances which would also serve at other temperatures. One of these, calcic nitrate, inverting at about 42·7°, is at present under investigation at this laboratory, and it is hoped that a complete temperature-scale of standards may be established. It is also hoped that with an admirable new air-thermometer, at present nearly finished in the Jefferson Physical Laboratory, a direct determination of the transition temperature of sodic sulphate may be made in terms of the hydrogen standard.

In brief, this preliminary paper shows that sodic sulphate "melts" at almost exactly 32·48° according to the mean mercury thermometer, and that this temperature is so easily obtained and so constant as to be of great use in the future of thermometry and thermostatics.

Chemical Laboratory of Harvard College, June, 1898.

* For practical details, pp. 203–206 should be consulted.

ART. XXI.—*Distribution and Quantitative Occurrence of Vanadium and Molybdenum in Rocks of the United States;* by W. F. HILLEBRAND.

[Read before the Geological Society of Washington, D. C., May 25th.]

ASIDE from its well-known mineral combinations, vanadium has long been known to occur in magnetites and other iron ores. Hayes in 1875 reported its occurrence in a great variety of rocks and ores. Quoting from Thorpe's Dictionary of Chemistry "it is said to be diffused with titanium through all primitive granite rocks (Dieulafait) and has been found by Deville in bauxite, rutile, and many other minerals, and by Bechi and others in the ashes of plants and in argillaceous limestones, schists, and sands . . . . ." It is further reported to comprise as V_2O_5 ·02–·07 per cent of many French clays, ·02–·03 per cent of some basalts, ·24 per cent of a coal of unknown origin and ·45 per cent of one from Peru, amounting to 38·5 per cent and 38 per cent of the ash and noted respectively by Mourlot and Torrico y Meca. Doubtless many other instances of its occurrence have been noted.

In Table I following is shown its quantitative occurrence and distribution in a large number and variety of igneous rocks of the United States arranged according to their silica contents; and in Table II the same data are given for a few of the component minerals separated from some of those rocks, while Table III shows its presence in metamorphosed and secondary rocks by a few examples of roofing slates and schists and especially by two composite samples representing 253 sandstones and 498 building limestones. These last two afford positive proof of its general distribution through rocks of those classes. Incidentally some information has been acquired as to molybdenum. Owing to lack of entire certainty as to its condition of oxidation, the vanadium is tabulated in terms of both V_2O_5 and V_2O_3, a point which will be reverted to later on. With very few exceptions the amount of each sample taken for analysis was five grams. The reagents used were carefully tested and found free from vanadium and molybdenum. Except Nos. 38, 39, 47, 52, and 53, by Dr. H. N. Stokes, all determinations are by myself.

TABLE I. *Igneous Rocks.*

No.	Name and locality of occurrence.	SiO_2 %	$V_2O_5=V_2O_3$ %	$V_2O_5=V_2O_3$ %	Mo %
1.	Melilite-nepheline basalt, Uvalde Co., Texas	38	·054	·045	
2.	Nephelinite, Uvalde Co., Texas	40	·042	·035	
3.	Saxonite, Douglas Co., Oregon	41·5	none	none	
4.	Diorite, Cecil Co., Maryland	44	·062	·052	none

No.	Name and locality of occurrence.	SiO_2 %	V_2O_5=V_2O_3 %	Mo %
5.	Gabbro, Adirondack region, N. York	45	·02	·017	
6.	Plagioclase basalt, Uvalde Co., Texas	45	·048	·04	
7.	Amphibole gabbro, Alpine Co., Calif.	46	·046	·038	none
8.	Plagioclase gneiss, Amador Co., Calif.	46·5	·033	·027	
9.	Diorite, Mitchell Co., N. Carolina	47	·05	·042	
10.	Porphyry, La Plata Co., Colorado	47	·06*	·05*	
11.	Amphibole gabbro, Tuolumne Co., Calif.	47	·024	·02	none
12.	Orthoclase-bearing basalt, Uvalde Co., Texas	48?	·048	·04	
13.	Orthoclase-bearing basalt, Uvalde Co, Texas	48	·02	·017	
14.	Norite, Cecil Co., Maryland	48	·023	·019	
15.	Gabbro, Union Co., Tennessee	48	·038	·032	
16.	Gabbro, Douglas Isld., Alaska	48	·055	·046	none
17.	Nepheline basanite, Colfax Co., N. Mexico	48·5	·044	·037	
18.	Olivine basalt, Kruzoff Isld., Alaska	49·5	·054	·045	none
19.	Diabase, Mt. Ascutney, Vermont	49·5	·034	·028	
20.	Phonolite, Cripple Creek, Colorado	50	·033	·027	
21.	Syenite lamprophyre, Prowers Co., Colorado	50·5	·04	·033	
22.	Augite-andesite porphyry, Electric Peak, Wyoming	50·5	·045	·038	
23.	Pyroxenic gneiss, Calaveras Co., Calif.	51·5	·10	·083	none
24.	Labradorite porphyrite, Michigamme iron district, Michigan	52·5	·048	·04	
25.	Pyroxenite, Cecil Co., Maryland	53	·04	·034	none
26.	Orendite, Sweetwater Co., Wyoming	54	·022	·018	
27.	Andesite, El Paso Co., Colorado	54?	·018	·015	tr.?
28.	Nepheline syenite, El Paso Co., Colorado	54·5	·022	·018	tr.?
29.	Diorite, Butte and Plumas Cos., Calif.	54·5	·037	·031	none
30.	Quartz diorite, Cecil Co., Maryland	55	·043	036	none
31.	Diorite, La Plata Co., Colorado	55·5	·038	·032	
32.	Camptonite? San Miguel Co., Colorado	55·5	lost, but considerable		
33.	Phonolite, Colfax Co, N. Mexico	56	tr.	tr.	
34.	Augite-bronzite andesite, Unga Isld., Alaska	56·5	·046	·038	none
35.	Andesite, El Paso Co., Colorado	57?	·025	·021	tr.?
36.	Spilosite, Michigamme iron district, Michigan	58	·03	·025	none
37.	Hornblende granite, Cecil Co., Maryland	58·5	·022	·018	none
38.	Latite, Tintic district, Utah	60	·007	·006	none
39.	Monzonite, Tintic district, Utah	60	·024	·02	tr.
40.	Diorite porphyry, La Plata Mts., Colorado	60·5	·02	·017	
41.	Trachyte-andesite tuff, Tuolumne Co., Calif.	62·5	·017	·014	
42.	Diorite, Douglas Isld., Alaska	63	·012*	·01*	none
43.	Rhyolite, San Miguel Co., Colorado	64·5	·004	·003	tr.
44.	Syenite, Mt. Ascutney, Vermont	65·5	tr.?	tr.?	
45.	Quartz-mica diorite, Tuolumne Co., Calif.	65·5	·013	·011	tr.
46.	Quartz monzonite, Calaveras Co., Calif.	67	·014	·012	none
47.	Rhyolite, Tintic district, Utah	69	·009	·008	tr.
48.	Quartz diorite, Amador Co., Calif.	69 5	·005	·004	tr.
49.	Trachyte, Highland Co., Virginia	69·5	tr.?	tr.?	
50.	Biotite granite, Amador Co., Calif.	70·5	tr.	tr.	tr.
51.	Rhyolite, Crater Lake, Oregon	71	·004	·003	ft. tr.
52.	Monzonite (altered), Tintic district, Utah	71	·021	·017	none
53.	Rhyolite quartz-porphyry, Tintic district, Utah	71·5	·016	·013	none
54.	Rock between rhyolite and dacite, Sutter Co., Calif.	71·5	tr.	tr.	
55.	Syenite porphyry, Mt. Ascutney, Vermont	73	none	none	
56.	Granite porphyry, Mt. Ascutney, Vermont	73·5	none	none	
57.	Granite, Union Co., Tennessee	76·5	none	none	

* Approximate.

TABLE II. *Component Minerals from certain of the above igneous rocks.*

No.	Name and source.	SiO_2 %	$V_2O_5 = V_2O_3$ %		Mo %
7[a].	Amphibole from 7	?	·075	·062	none
11[a].	Amphibole from 11	46	·044	·037	none
21[a].	Pyroxene from 21	51.5	·043	·036	
23[a].	Biotite from 23	36.5	·153	·127	none
29[a].	Amphibole from 29	50	·08	·066	
45[a].	Biotite from 45	?	·057	·048	none
46[a].	Biotite from 46	35·5	·08	·066	

TABLE III. *Miscellaneous.*

No.	Name and locality of occurrence.	SiO_2 %	$V_2O_5 = V_2O_3$ %		Mo %
58.	Epidotic schist, Mitchell Co., N. Carolina	48	·057	·047	
59.	Quartz schist, Madera Co., Calif.	79	tr.	tr.	
60.	Serpentine, Connecticut Valley, Massachusetts	38·5	none	none	
61.	Sea green roofing slate, West Pawlet, Vermont	68	·017	·014	
62.	Two red roofing slates (equal parts), Washington Co., New York	67 56	·008	·007	
63.	253 sandstones	78·5	·003	·003	
64.	498 building limestones	14	·004	·004	

Of the igneous rocks specimens were so selected as to represent not only many widely separated localities, but also numerous varieties from the least siliceous up to those high in silica, in order to ascertain whether a preconceived opinion that the vanadium accompanied chiefly the less siliceous rocks was well founded or not. The choice was, however, confined largely to those rocks analyzed in this laboratory within the past three or four years of which a supply of powder remained after the original analyses had been completed, and hence the list is perhaps not fully representative. Nevertheless it permits of drawing certain conclusions, the chief of which is that the vanadium predominates in the less siliceous igneous rocks and is absent or nearly so in those high in silica. The inference, based on the existence of the mineral roscoelite, classed as a vanadium mica, at once suggests itself, that the ultimate source of the vanadium may be one or more of the heavier silicates such as the biotites, pyroxenes, and amphiboles, and a few tests on all the available mineral separation products lend strong support to this view. For instance, the amphibole gabbros 7 and 11 show ·038 per cent and ·02 per cent V_2O_3, while the amphiboles 7[a] and 11[a] separated from them give ·062 per cent and ·037 per cent; the pyroxenic gneiss 23 shows ·083 per cent against ·127 from its contained biotite 23[a]; the diorite 29 with ·031 per cent contains an amphibole 29[a] with ·066 per cent; from ·011 per cent in the quartz-mica diorite 45 and ·012 per cent in the quartz monzonite 46 the percentages rise to ·048 and ·066 in their separated biotites 45[a] and 46[a]. The pyroxene

21[a] shows, however, practically the same amount as its mother rock, the syenitic lamprophyre 21.

In most of these cases, notably the last one, the vanadium in the separated mineral is not sufficiently in excess of that in the rock from which it was taken to account for all of that found in the latter. Hence, if the determinations are correct it must also be a constituent of some other mineral than the one analyzed. In roscoelite the trivalent condition of vanadium corresponding to the oxide V_2O_3 is now recognized as probable, although Roscoe's analysis reports V_2O_5 and Genth's an oxide intermediate between V_2O_3 and V_2O_5. This assumption seems to be necessary if the mineral is to be regarded as a mica, and it is then doubtless the equivalent of trivalent iron or aluminum. It would then be natural to look for it in the aluminous or ferric silicates of igneous rocks, certain biotites, pyroxenes, and hornblendes, and its absence in such minerals as serpentine and chrysolite, as shown by analyses 3 and 60, appears natural enough.

Few and inconclusive as the above comparisons are, they seem to favor strongly this view as to the source of the vanadium and in a measure are confirmatory of the observation of Hayes (Proc. Am. Ac., x, 294, 1875), who rather indefinitely associates it with phosphorus and proto-salts of iron and manganese, which are usually more prominent components of basic than of acid rocks.

We are probably justified by the evidence in tabulating the vanadium as V_2O_3 in analyses of igneous and some metamorphic rocks which have undergone little or no oxidation, but with sandstones, clays, limestones, etc., which are of more or less decided secondary origin, this is probably not the case. The probabilities are there largely in favor of its acid character and the existence of various vanadates of calcium, iron, aluminum, etc., in which case it should appear in analytical tables as V_2O_5.*

It was not until the greater part of the above tests had been finished that any careful attempt was made to identify molybdenum as well as vanadium. From the evidence gathered during the later part of the work it would seem that molybdenum when it does occur is a much less important constituent quantitatively than vanadium, and that unlike the latter it accompanies the more acid rocks. Molybdenite is a well known accessory constituent of some granites, etc., but in the above instances its amount was extremely small and no hint was obtained as to its state of combination.

* In the regular course of analysis vanadium will be weighed with alumina, iron, titanium, etc., since it is precipitated by both ammonia and sodium acetate in presence of those and other metals, hence the alumina percentages in

Chemical method employed.

In conclusion it is proper to outline the method by which the foregoing tests were carried out and to indicate the precautions that must be observed in order to insure good results.

Quite a number of workers have busied themselves with the problem of vanadium estimation in ores and rocks, particularly magnetites and other iron ores, and the methods used have been often diverse in parts if not altogether. There is nothing absolutely novel in the following except that chromium and vanadium when together need not be separated, but are determined, the former colorimetrically, the latter volumetrically in the same solution as detailed elsewhere.*

Five grams of the rock are thoroughly fused over the blast with twenty of sodium carbonate and three of sodium nitrate. After extracting with water and reducing manganese with alcohol it is probably quite unnecessary, if the fusion has been thorough, to remelt the residue as above, though for magnetites and other ores containing larger amounts of vanadium than any of these rocks, this may be necessary, as Edo Claassen has shown.† The aqueous extract is next nearly neutralized by nitric acid, the amount to be used having been conveniently ascertained by a blank test with exactly twenty grams of sodium carbonate, etc., and the solution is evaporated to approxi-

nearly all rock analyses heretofore made are subject to correction for the vanadium the rock may have held. This correction is of course to be made in terms of V_2O_5 and not of V_2O_3.

All determinations of iron are likewise affected by its presence whether as V_2O_5 or V_2O_3. As V_2O_3 it will make the FeO appear too high in the proportion V_2O_3: 4FeO, or 150·8: 288, an error which becomes appreciable in some of the basic rocks and amounts to ·25 per cent in the biotite 23ª. As V_2O_5 the FeO will not be affected, but in either condition the Fe_2O_3 will need correction and to a different extent, according as the titration of iron is made after reduction by hydrogen sulphide or by hydrogen. If the former is used, as should always be the case in presence of titanium the vanadium is reduced by it to V_2O_4, which in its action on permanganate is equivalent to two molecules of FeO representing one of Fe_2O_3, or only one-half as great as the influence on the FeO titration of the same vanadium as V_2O_3. An example will make this clear.

Found 2·50 per cent apparent FeO in a rock containing ·13 per cent V_2O_3
Deduct ·25 per cent FeO equivalent in its action on $KMnO_4$ to ·13 V_2O_3
Leaving 2·25 per cent FeO corrected.
Found 5·00 per cent apparent total iron as Fe_2O_3 in the same rock.
Deduct ·14 per cent Fe_2O_3 corresponding to ·13 per cent V_2O_3
Leaving 4·86 per cent corrected total iron as Fe_2O_3
Deduct 2·50 per cent Fe_2O_3 equivalent to 2·25 per cent FeO
Leaving 2·36 per cent Fe_2O_3 in the rock.

Failure to correct for the vanadium in both cases would have made the figures for FeO and Fe_2O_3 respectively 2·50 and 2·22 instead of 2·25 and 2·36 as shown above.

* Jour. Am. Chem. Soc., xx, pp. 454 and 461, 1893.

† Am. Chem. Jour., viii, 437.

mate dryness. Care should be taken to avoid overrunning neutrality because of the reducing action of the nitrous acid set free from the nitrite, but when chromium is present it has been my experience that some of this will invariably be retained by the precipitated silica and alumina, though only in one case have I observed a retention of vanadium, it being then large. The use of ammonium nitrate instead of nitric acid for converting the sodium carbonate into nitrate did not seem to lessen the amount of chromium retained by the silica and alumina.

As a precautionary measure therefore, and always when chromium was to be estimated also, the silica and alumina precipitate was evaporated with hydrofluoric and sulphuric acids, the residue fused with a little sodium carbonate and the aqueous extract again nearly neutralized with nitric acid and boiled for a few moments, the filtrate being added to the main one.

Mercurous nitrate was now added to the alkaline solution in some quantity so as to obtain a precipitate of considerable bulk containing chromium, vanadium, molybdenum, tungsten, phosphorus, and arsenic, should all happen to be in the rock, and also an excess of mercurous carbonate to take up any acidity resulting from the decomposition of the mercurous nitrate. Precipitating in a slightly alkaline instead of a neutral solution renders the addition of precipitated mercuric oxide unnecessary for correcting this acidity. If the alkalinity, as shown by the formation of an unduly large precipitate, should have been too great, it may be reduced by careful addition of nitric acid until an added drop of mercurous nitrate no longer produces a cloud.

After heating and filtering, the precipitate is ignited in a platinum crucible after drying and removing from the paper to obviate any chance of loss of molybdenum and of injury to the crucible by reduction of phosphorus or arsenic. The residue is fused with a very little sodium carbonate, leached with water, and the solution if colored yellow filtered into a graduated flask of 25 or more cubic centimeters capacity. The chromium is then estimated accurately in a few minutes by comparing with a standard alkaline solution of potassium monochromate.* Then, or earlier in absence of chromium, sulphuric acid is added in slight excess and molybdenum and arsenic together with occasional traces of platinum are precipitated by hydrogen sulphide, preferably in a small pressure bottle.† If the color of the precipitate indicates absence of arsenic, the filter with its

* Jour. Am. Chem. Soc., xx, 454, 1898.

† From a sulphuric solution the separation of molybdenum by hydrogen sulphate is much more rapid and satisfactory than from a hydrochloric solution.

contents is carefully ignited in porcelain and the delicate sulphuric acid test for molybdenum is applied.

The filtrate, in bulk from 25 to 100^{cc}, is boiled in a current of carbon dioxide to expel hydrogen sulphide, and titrated at a temperature of 70–80° C. with a very dilute solution of permanganate representing about one milligram of V_2O_5 per cubic centimeter as calculated from the iron strength of the permanganate, one molecule of V_2O_5 being indicated for each one of Fe_2O_3. One or two checks are always to be made by reducing again in a current of sulphur dioxide gas, boiling this out in a current of carbon dioxide again, and repeating the titration.

As shown in a previous paper* the presence of even thirty times as much Cr_2O_3 as V_2O_5 does not prevent a satisfactory determination of the vanadium if the precautions therein given are observed, provided there is present not less than ½–1 mg. of V_2O_5 in absolute amount. In absence of chromium less than half a milligram can be readily estimated. The phosphoric acid almost invariably present does not affect the result.

In case the volume of permanganate used is so small as to make doubtful the presence of vanadium, it is necessary to apply a qualitative test which is best made as follows: The solution is evaporated and heated to expel excess of sulphuric acid, the residue is taken up with two or three cubic centimeters of water and a drop or two of dilute nitric acid, and a couple of drops of hydrogen peroxide are added. A characteristic brownish tint indicates vanadium. Unless the greater part of the free sulphuric acid has been removed the appearance of this color is sometimes not immediate and pronounced, hence the above precaution.

The above is a surer test to apply than the following: Reduce the bulk to about ten cubic centimeters, add ammonia in excess and introduce hydrogen sulphide to saturation. The beautiful cherry-red color of vanadium in ammonium sulphide solution is much more intense than that caused by hydrogen peroxide in acid solution, but the action of ammonia is to precipitate part or all of the vanadium with the chromium or aluminum that may be present or with the manganese used in titrating, and ammonium sulphide is unable to extract the vanadium wholly from these combinations. Usually, however, the solution will show some coloration, and addition of an acid precipitates brown vanadium sulphide, which can be collected, ignited and further tested if desired.

* Jour. Am. Chem. Soc., xx, 464, 1898.

Summary of Results.

Vanadium occurs in quite appreciable amounts in the more basic igneous and metamorphic rocks, up to ·08 per cent or more of V_2O_3, but seems to be absent or nearly so from the highly siliceous ones. The limited evidence thus far obtained points to the heavy ferric-aluminous silicates as its source—the biotites, pyroxenes, amphiboles. As opportunities offer further evidence will be accumulated and it is hoped that other chemists will lend their aid.

Limestones and sandstones appear to contain very small amounts of vanadium, as shown by analyses of a composite sample of each aggregating over 700 different occurrences.

From the few tests for molybdenum it appears as if this element were confined to the more siliceous rocks. It is present in no observed case in amount sufficient for quantitative measurement when operating on five grams of material.

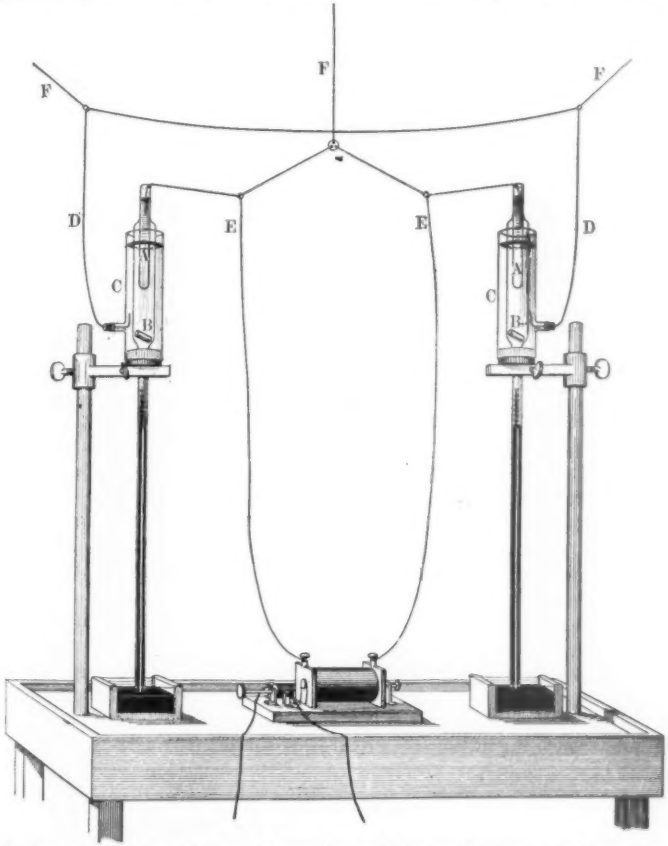
Laboratory of the U. S. Geological Survey,
Washington, D. C., May 1898.

Note. Since the above was written a few tests have been made on minerals of which powdered samples were at hand. A phlogopite from Burgess, Canada, gave ·007 per cent V_2O_3. Mica from Laurel Hill, Georgia, gave ·026 per cent V_2O_3. Protovermiculite from Magnet Cove, Ark., gave ·04 per cent V_2O_3. Hallite from Chester Co., Pa., gave ·01 per cent V_2O_3. Jeffersonite from Franklin, N. J., gave none, and a non-ferruginous amphibole from St. Lawrence County, N. Y., gave a faint trace.

ART. XXII. — *On Electrosynthesis;* by W. G. MIXTER. (Second paper.)

[Contributions from the Sheffield Laboratory of Yale University.]

THE apparatus described in the first paper* was used in the work. For convenience the figure of it is reproduced. The gases in the two eudiometers at the commencement of an experiment were, unless otherwise stated, at nearly the same pressure, which was less than 200^{mm} of mercury. The volumes



of the gases are either given in cubic centimeters reduced to 0° C. and 760^{mm} pressure, or in numbers expressing the proportional number of volumes of each gas. Solid potassium

* This Journal, vol. iv, p. 51.

hydroxide was used to absorb water in the eudiometer containing hydrogen and oxygen, and a saturated solution was used in the other eudiometer unless a different reagent is mentioned. The same empirical measure was employed as before, which is the amount of hydrogen and oxygen combining in one eudiometer while the gases in the other eudiometer also combined, the same current passing through both eudiometers. The numerous details common to all of the experiments are omitted, while any modification is fully described. Many experiments were made while the work was in progress with electrolytic hydrogen and oxygen in both eudiometers in order to find if the apparatus was working well, to test the method more fully and to study the conditions affecting the rate of change produced by a given current through the apparatus.

The view expressed in the first paper, that heat resulting from the combination effected by the feeble glow discharge does not cause further combination, is supported by the following results. The jacket tube C shown in the figure was replaced by a wire wound twice around B, opposite the lower end of A and connected with the wire D. With this arrangement the discharge is concentrated but without sparks, and the glow is more intense than in the jacketed tube. The eudiometers in the following tests contained hydrogen and oxygen:

	Diffused discharge.	Concentrated discharge.
Exp. 1	1·88^{cc} combined.	1·89^{cc} combined.
" 2	2·55 "	2·67 "

The heat of combustion was the same in the two tubes as equal quantities of gases united, but it was distributed through several times the volume of gas in one case than in the other. If the heat resulting from the action in the feeble glow discharge causes chemical union, we should expect in the other case where the temperature is obviously higher, since the same amount of heat is generated in a smaller volume, that the resultant combination would be greater. As it was not found to be so, we conclude that the heat of combination does not cause further union of the gases. If, however, the discharge is sufficiently powerful we should expect a different result. This was found to be so, for with a stronger current through the apparatus the concentrated discharge caused three times as much combination as the diffused discharge.

When a solution, instead of solid potassium hydroxide, is used in a eudiometer through which a current is passing, a feeble spark is perceptible if the finger is held near the mercury in the trough, but none is felt when a eudiometer does not contain a solution. For the following experiments the sides of one eudiometer were coated with a saturated solution of potassium hydroxide from the top of the mercury column nearly to the inner tube A:

	With solution of KOH.	With solid KOH.
Exp. 1	2·79^{cc} combined.	2·63^{cc} combined.
" 2	6·30 "	6·64 "

These results show that the presence of a solution does not influence the rate of change produced by the current through hydrogen and oxygen.

For a time the coil used gave a feeble and intermittent glow in one eudiometer and a fairly steady one in the other. Upon changing the direction of the primary current these effects were frequently reversed. The intermittent discharge in a eudiometer caused less oxygen and hydrogen to unite than the steady discharge. Moreover, the rate of combination was much slower than had been obtained in previous experiments with the same coil actuated by the same current. Two other smaller coils which have been in the chemical laboratory many years gave the same abnormal results. An examination of the first coil mentioned showed that some of the connections were corroded. When put in order it gave good results again. Later a new and larger coil yielding a 4-inch spark was used with satisfactory results, the break being adjusted to give a spark of 1 to 2 centimeters.

A number of experiments were tried with hydrogen and oxygen at widely different pressures in the two eudiometers to find if there is any simple relation between the rate of combination and pressure. The results, however, only confirm the statement in the first paper that the higher the pressure the more rapid the combination.

In the previous paper allusion was made to the fact, when the eudiometers were near together and the coil was connected with only one of them, that a glow sometimes appeared in the other. To find if combination occurs under such conditions one eudiometer containing oxygen and hydrogen under a pressure of 10·9^{mm} was placed 6 centimeters from the other eudiometer containing air at a pressure of 3^{mm}. The two were insulated by wood and glass. The mercury in the trough of the one containing air and the water in the tube A were connected with the coil actuated by a current of 3 amperes. The discharge was brilliant and striated, and caused a distinct glow in the oxygen and hydrogen visible in a dark room when the light of the other tube was shut off by a screen of black paper. The glow was much brighter on the side towards the screened tube. After two hours the pressure had fallen 2·3^{mm}, and the gas, which was originally 1·64^{cc}, was reduced to 1·32^{cc}, the water formed being taken up by solid potassium hydroxide. When the eudiometers were 13 centimeters apart the combination was perceptible but much slower. It is evident that a very feeble electric action causes the oxidation of hydrogen, and

this suggests that the hydrogen continually passing into the atmosphere but not accumulating may be at least to a considerable extent oxidized by the electricity of the aurora. As stated in the first paper, vapor of water is decomposed by the glow discharge. To find the amount of decomposition and to find how completely hydrogen and oxygen combine in the presence of water, vapor of water in one eudiometer and moist hydrogen and oxygen in the other were submitted to the glow discharge produced by a current of one ampere in the primary of the coil. In four hours the pressure was the same in both tubes and $0{\cdot}8^{mm}$ greater than the pressure of water vapor at the temperature, which was $17{\cdot}8°$. With a current of 1·8 amperes the pressure increased $0{\cdot}9^{mm}$. The results show that the electrolytic hydrogen and oxygen used almost completely combined to form water, also that with a given current through the apparatus as described a state of equilibrium in the gases results.

Ammonia and Oxygen.

A mixture of $23{\cdot}6^{cc}$ of oxygen and $28{\cdot}8^{cc}$ of ammonia contracted $23{\cdot}9^{cc}$, while one of hydrogen and oxygen contracted $18{\cdot}6^{cc}$. The nitrogen gas remaining after the electric discharge ceased to cause further contraction in the gaseous mixture was only $\frac{5}{6}$ of the nitrogen supplied by the ammonia, the remainder having entered into a non-gaseous compound. This was ammonium nitrite, which formed a white coating on the sides of the eudiometer, and which reacted for nitrous acid with the usual tests. Nitrate was probably also formed. The relative proportions of the two reactions may be represented by the equations

$$10NH_3 + 7\tfrac{1}{2}O_2 = 5N_2 + 15H_2O$$
$$2NH_3 + 1\tfrac{1}{2}O_2 = NH_4NO_2 + H_2O$$
24 vols. 18 vols. 10 vols.

In the experiment 100 volumes of oxygen and hydrogen to 128 volumes of ammonia and oxygen disappeared; as 10 volumes of nitrogen remain for every 42 volumes of ammonia and oxygen reacting, we have $128 \times \frac{42}{32} = 168$ for the total number of volumes of the two gases combined. Of these 88 are ammonia oxidized, 72 oxygen, and 8 are ammonia combined in the nitrite.

In the second experiment there was more of a deposit of ammonium nitrite than in the first and the residual nitrogen was $\frac{3}{4}$ of that supplied by the ammonia taken, and for 100 volumes of oxygen and hydrogen 141 volumes of the mixture of ammonia and oxygen disappeared; or allowing for the nitrogen gas 179, consisting of 89 volumes of ammonia oxidized, 13 combined in nitrite and 77 of oxygen.

Amines and Oxygen.

A mixture of 20^{cc} of oxygen and 10^{cc} of methylamine gas contracted 12·4^{cc}, while hydrogen and oxygen contracted 6·4^{cc}, a ratio of 194 to 100. Assuming the reaction to be

$$\underset{\text{4 vols.}}{2NH_2CH_3} + \underset{\text{9 vols.}}{4\tfrac{1}{2}O_2} = \underset{\text{2 vols.}}{N_2} + 2CO_2 + 5H_2O$$

and allowing for the nitrogen, we have $194 \times \frac{3}{11} = 229$ volumes, of which 70 are methylamine and 159 are oxygen. The solution of potassium hydroxide after the experiment reacted for nitrous acid, and assuming

$$\underset{\text{4 vols.}}{2NH_2CH_3} + \underset{\text{13 vols.}}{6\tfrac{1}{2}O_2} = 2NO_2 + 2CO_2 + 5H_2O$$

the 194 volumes consist of 46 of methylamine and 148 of oxygen. The two reactions occur simultaneously and we may consider that methylamine is oxidized somewhat slower than hydrogen.

The ratio observed between a mixture of hydrogen and oxygen and one of dimethylamine and oxygen was 100 to 300 volumes with formation of nitrous acid. Calculated as for methylamine we find 70 volumes of dimethylamine oxidized on the assumption that all of the nitrogen is set free, and 57 volumes, assuming the nitrogen to form NO_2.

Trimethylamine and oxygen gave a very different result from the two preceding, as no nitrous acid was detected. It may have been formed and decomposed by the amine. For 100 volumes of hydrogen and oxygen 265 of trimethylamine and oxygen combined, consisting of 42 of trimethylamine and 223 of oxygen.

A mixture of aniline vapor and oxygen at 30° C. and 100^{mm} pressure contracted very slowly when subjected to the glow discharge and a brown condensation product was deposited on the sides of the tube. No nitrous acid was detected in the products.

Cyanogen and Oxygen.

A mixture of one volume of dry cyanogen and two volumes of oxygen was subjected to the glow discharge. For a time it increased a little in volume, and afterwards slowly contracted to about the original bulk of the mixed gases. A solution of barium hydroxide was added to absorb carbon dioxide and any cyanogen left. The gases remaining after this treatment contracted much and when again subjected to the discharge more barium carbonate formed. Two tests were made, using potassium hydroxide solution as an absorbent, with similar but unsatisfactory results. Scarcely more than a trace of nitrous acid was detected. The changes caused by the glow discharge are too complicated to admit of an accurate comparison with the

rate of change in hydrogen and oxygen, but the observations made indicate that cyanogen is oxidized faster than hydrogen. The products are carbon monoxide and dioxide, free nitrogen and a small proportion of condensation products and oxides of nitrogen. It was found that pure cyanogen gas condenses very slowly with formation of a brown product when subjected to the glow discharge.

Nitrous Oxide. 1st Experiment.

	Nitrous oxide.	Change.	Hydrogen and oxygen.	Change.
	18·46cc		30·cc	
1st hour....	18·77	+0·31cc	25·5cc	−4·5cc
2d "	19·56	+0·79	21·5	−4·
3d "	20·17	+0·61	17·6	−3·9

The saturated solution of potassium hydroxide on the sides of the eudiometer containing the nitrous oxide became dry with the formation of nitrite and probably nitrate.

2d Experiment.—A solution of pyrogallic acid in potassium hydroxide was used to absorb the oxygen set free from the nitrous oxide. 12·85cc of the latter gas were changed by the discharge to 11·9cc, while 5·6cc of hydrogen and oxygen combined.

3d Experiment.—Nitrous oxide increased 1·7cc in half an hour while hydrogen and oxygen contracted 2·8cc. During the next half hour the volume of the gas in tube originally containing nitrous oxide remained unchanged, while 3·3cc of hydrogen and oxygen united.

The results show that the glow discharge causes complicated changes in nitrous oxide. The increase in volume of 1·7cc corresponds to 3·4cc according to the equation $N_2O = N_2 + O$; that is, 100 volumes of hydrogen and oxygen combined and 121 volumes of nitrous oxide decomposed. The other experiments show a much lower result for the oxide, but the volume change was not observed until the action of the current had continued an hour or longer. The contraction in the second experiment shows that some of the nitrous oxide is changed according to one or the other of the equations

$$3N_2O = N_2O_3 + 2N_2$$
$$4N_2O = 2NO_2 + 3N_2$$

Nitrous Oxide and Hydrogen.

Two experiments were made with a mixture containing a little more hydrogen than nitrous oxide. For 100 volumes of hydrogen and oxygen combined the mixture of nitrous oxide and hydrogen contracted respectively 54 and 58, or an average of 56 volumes. The potassium hydroxide in the eudiometer

reacted for nitrite. As it has been shown that nitrous oxide undergoes little change in volume when subjected to the glow discharge, we may consider the change in volume when hydrogen is present to be

$$N_2O + H_2 = N_2 + H_2O$$

and that 56 volumes of hydrogen were oxidized by 56 of nitrous oxide. As the latter is endothermic it is remarkable that it does not oxidize hydrogen as rapidly as free oxygen.

Nitric Oxide.

When nitric oxide in a eudiometer containing a solution of potassium hydroxide is subjected to the glow discharge the volume of the gas contracts rapidly at first, then slowly until the discharge causes no further change and nitrogen is left. In the experiments there was one volume of the residual gas for 5, 4·96, 5·4, 5·3 and 4·88, a mean of 5·11 volumes of nitric oxide taken. The change is according to the equation

$$\underset{10\text{ vols.}}{5NO} = NO_2 + \underset{2\text{ vols.}}{N_2O_3} + N_2$$

In three experiments for every 100 volumes of hydrogen and oxygen combined 153, 160 and 167, an average of 160 volumes, disappeared; allowing for the nitrogen set free, we have $160 \times \frac{5}{4} = 200$ volumes of nitric oxide involved in the change. Assuming that $\frac{2}{5}$ of the nitric oxide is decomposed into nitrogen and oxygen, the latter combining with nitric oxide to form higher oxides, we have $\frac{2}{5}$ of $200 = 80$ volumes of nitric oxide decomposed to 100 of hydrogen and oxygen combined. It is highly probable that the glow discharge changes nitric oxide directly into higher oxides. If so the relative change caused by the electricity is greater than that indicated by the calculation.

Nitric Oxide and Hydrogen.

A mixture of equal volumes of nitric oxide and hydrogen contracted in comparison with 100 volumes of hydrogen and oxygen in two experiments respectively, 91 and 92 volumes. This is about $\frac{9}{16}$ of the contraction observed when nitric oxide alone was used, and the results indicate that the hydrogen present retarded the action by diluting the gas. The potassium hydroxide in the eudiometer reacted for nitrite, showing that hydrogen did not take up all of the oxygen of the nitric oxide dissociated. This was to be expected, as nitric oxide combines with free oxygen more readily than hydrogen at common temperatures. The experiments do not show that hydrogen was oxidized. Assuming, however, that all of the contraction in volume was due to the reaction $NO + H_2 = N + H_2O$, we find that nitric oxide does not oxidize hydrogen as rapidly as does oxygen.

Nitric Oxide and Carbonic Oxide.

Experiment 1.—Equal volumes of mixed nitric oxide and carbonic oxide contracted 6^{cc} and hydrogen and oxygen 3·8^{cc}.

Experiment 2.—A mixture of 6·5^{cc} of nitric oxide and 8^{cc} of carbonic oxide left 8·6^{cc} of gas when the electric discharge caused no further contraction.

Experiment 3.—A solution of barium hydroxide used as an absorbent became but slightly turbid when the glow discharge acted on a mixture of nitric and carbonic oxide.

These results show that the contraction of the mixed oxides is about the same as that of nitric oxide, and that the glow discharge acts chiefly on the nitric oxide in the mixture, also that some carbonic oxide is oxidized.

Molecular Changes.

The following table is based on the change in volumes observed, and one volume of hydrogen and oxygen is considered to contain 100 molecules.

Gases used.	Molecules reacting.	Molecules oxidized.		Molecules of oxygen consumed.
Hydrogen and oxygen	100	H_2	67	33
Ammonia "	168	NH_3	88	72
" "	179	"	89	77
Methylamine "		NH_2CH_3	46 to 70	
Dimethylamine "		$NH(CH_3)_2$	57 to 70	
Trimethylamine "	265	$N(CH_3)_3$	42	213
Hydrogen and nitrous oxide,	112	H_2	56	
" nitric "	Little if any hydrogen oxidized.			
Carbonic oxide and nitric oxide.	Some carbonic oxide oxidized.			

Cyanogen is probably more rapidly oxidized than hydrogen, but further work is needed to settle this point. It is probable that more molecules of nitrous oxide are changed than of hydrogen and oxygen combined. In the case of nitric oxide, if we suppose that the glow discharge simply separates the compound into its elements, we find that 80 molecules are decomposed to 100 molecules of hydrogen and oxygen combined. This supposition is equivalent to the assumption that higher oxides are not formed by the direct combination of two or three molecules of nitric oxide with separation of nitrogen. It does not appear that the nature of the reaction can be determined by experiment.

The glow discharge used is too feeble to oxidize nitrogen, but when it causes the oxidation of nitrogenous compounds the nitrogen is more or less oxidized. In conclusion it may be stated that a mixture of carbon disulphide and oxygen at a pressure of 138^{mm} was exploded by the feeble glow discharge; also that the synthesis of formic acid from carbonic oxide and water vapor and from hydrogen and carbon dioxide was found to be much slower than the synthesis of water.

Art. XXIII.—*Notes on species of Ichthyodectes, including the new species I. cruentus, and on the related and herein established genus Gillicus;* by O. P. Hay, Ph.D.

Ichthyodectes hamatus Cope.

Cope, 1872, Proc. Amer. Philos. Soc., vol. xii, p. 340; 1875, Cretaceous Vertebrates, p. 209, pl. xlvi, figs. 5, 5*a*.

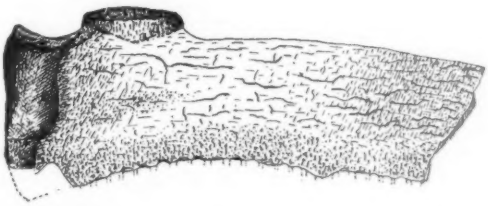
Of this species I possess two nearly complete dentaries. The tooth-line has a length of 100^{mm}. One dentary has 27 teeth; the others 28. Prof. Cope states that the mandibular in his possession displayed 25 teeth, but it is quite probable that there is considerable individual variation in the number. The form of the jaw and the presence of the upturned symphysial hook indicates that my specimens belong to Cope's *I. hamatus*. The teeth are closely arranged and they show a peculiarity of form and setting that has not been noticed by Prof. Cope. This peculiarity is found in the fact that the teeth are elliptical in section, with the long axis of the section placed obliquely to the axis of the tooth-line, its outer end being thrown forward. The longer axis will average close to 5^{mm} in length, the shorter about 3^{mm}. The alveolar border is somewhat scooped out on the inner side just behind the hook, and just here the teeth are smaller than elsewhere. On the hook itself there are two teeth. The enamel is smooth.

Ichthyodectes cruentus sp. nov.

Figs. 1 and 3.

This supposed new species is founded primarily on a somewhat imperfect left maxilla which came from Butte Creek

1.



Canyon region in western Kansas. I have also a nearly perfect dentary and portions of one or two others which apparently belong to the same species. Of the maxilla, the anterior extremity, including the anterior condyle, is wanting, and also the distal extremity (fig. 1 × $\frac{2}{3}$).

This species appears to be nearest to Prof. Cope's *I. anaides*. It differs, however, in having larger teeth, as well as in some other respects. In my possession is the maxilla of a specimen of the last named species which has the depth from the upper surface of the palatine condyle to the tooth-line equal to that of *I. cruentus*. In this maxilla of *I. anaides* I find about 10 teeth to the inch; in *I. cruentus* there are only 7 teeth to the inch. The teeth being larger, we find that the alveolar border of the maxillary is thicker than in *I. anaides*. Indeed, the whole bone is of heavier construction. In *I. anaides* the mesial surface is nearly flat, or even has a wide shallow groove some distance below its upper border. In *I. cruentus* the mesial surface is decidedly convex. In *I. anaides* the upper border is flattened at right angles with the outer surface of the bone; while in *I. cruentus* it is gradually rounded off, from a sharp outer edge, into the mesial surface.

The palatine condyles of the maxillæ of the two species are quite different. Figure 2 represents that of *I. anaides*, of natural size. Figure 3 shows that of *I. cruentus*, also of natural size. Further descriptions are not required.

2.

3.

From *I. ctenodon* (Cope, Cret. Vert., p. 208, pl. xlvi, figs. 1–4) this species differs in having a high, not a low, palatine condyle. The maxillary of *I. ctenodon* is said to be a rather thin and narrow bone.

I. hamatus has a maxillary whose dental border is very concave. According to Cope's figure, there must have been 10 or 12 teeth to the inch (Cope, Cret. Vert., p. 209, pl. xlvi, fig. 5).

I. prognathus also must have had smaller teeth, judging from Cope's figure of the premaxillary (Cope, Cret. Vert., p.

210, pl. xlvi, fig. 6). Cope also states that the palatine condyle of *I. prognathus* reached "a point above the middle of the alveolar margin of the premaxillary." This is certainly not true of *I. cruentus*.

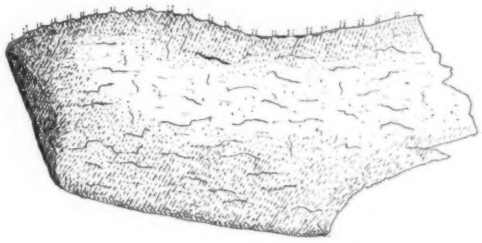
In *I. multidentatus* (Cope, Cret. Vert., p. 212) the teeth are small, about 12 to the inch, and are marked by ridges and grooves.

In *I. goodeanus* (Cope, Proc. Amer. Philos. Soc., xvii, p. 176) the maxillary tooth-line is directed upward and inward in front and then becomes convex. The palatine condyle is said to be not protuberant. *I. acanthicus* (Cope, loc. cit., p. 177) is a small species which has the dentary teeth attenuated and curved inward at the apex.

Newton has given descriptions of two English species of this genus, *I. minor* (Egerton) and *I. elegans* Newt. (Quart. Jour. Geol. Soc., xxxiii, p. 520.) *I. minor* has a very straight mandibular tooth-line; *I. elegans* has extremely long, forwardly projecting mandibular teeth.

Length of portion of maxilla of *I. cruentus* here described, 100^{mm}; depth at middle of palatine condyle, 34^{mm}; depth at point 34^{mm} behind the palatine condyle, 28^{mm}.

4 × ¾.



Where the bone is fractured near its distal end there are shown in its interior large medullary cavities, now occupied by calcite.

The dentary bone which I regard as belonging to this species is shown by figure 4. Nearly the whole of the tooth-line is present, perhaps not more than 3 or 4 teeth being missing. This indicates that there were 30 teeth. The alveolar border is sinuous, being strongly concave behind the middle and rising further behind. In front of the concavity the border is convex, and then descends to the symphysis. The convexity appears to correspond to the concavity of the alveolar border of the maxilla; while the symphysial descent corresponds to the downward slope of the anterior end of the maxilla, which

slope was probably continued forward by the premaxillary. In a fragment of the dentary which I regard as belonging to this species there is preserved one tooth complete. It is straight, 7^{mm} high and the enamel is smooth.

Ichthyodectes arcuatus Cope and *I. polymicrodus* Crook.

Portheus arcuatus Cope, 1875, Cret. Vert., pp. 193, 204, 274, pl. xlvii, figs. 7–9 (figures doubtful).

Ichthyodectes arcuatus Cope, Proc. Amer. Philos. Soc., vol. xvii, p. 177; 1892, Amer. Nat., vol. xxvi, p. 942.

Ichthyodectes polymicrodus Crook, A. J., 1892, Palæontographica, vol. xxxix, p. 112, pl. xvi.

In *Palæontographica*, as above cited, Dr. Crook has described as new a species of fossil fish from the Cretaceous deposits of western Kansas and has bestowed on it the name *Ichthyodectes polymicrodus*. This species he compares with Prof. Cope's *Ichthyodectes multidentatus* and concludes that the two are distinct species. In this conclusion he is doubtless correct, because of the evident difference in the size and number of teeth in the two forms. I can, however, with difficulty accept Dr. Crook's statement that the maxilla of his species possessed 24 teeth to the centimeter. This might possibly be true of the distal end of the maxilla, where they become very small, but not for the anterior end, even according to Dr. Crook's figure. In Cope's species, *I. multidentatus*, there were only 5 teeth to the centimeter.

In a review of Dr. Crook's paper (Amer. Naturalist, vol. xxvi, p. 941) Prof. Cope claims that Dr. Crook's species is the same as that originally described by Cope as *Portheus arcuatus*, and which is retained by Crook in *Portheus*, but transferred by Cope to *Ichthyodectes*. It is hard to understand why the species was originally placed in *Portheus*, since its dentition is very different from that of this genus. There appears to have been some confusion in Prof. Cope's mind regarding this species. It was founded on somewhat imperfect maxillary and palatine bones, and the original description given of it pertained to these bones. (Cret. Vert., p. 204.) On page 274 of the *Cretaceous Vertebrates*, under this species, Cope refers to plate xlvii, figs. 7–9. When we turn to this plate we find figures of what appears to be an *Ichthyodectes*. On the plate they are said to belong to *? Portheus arcuatus;* while in the explanation of the plate they are referred to *Portheus? arcuatus*, We are therefore unable to say whether Prof. Cope was in doubt as to the species or the genus. On page 220 B, line 16, two of the same figures are mentioned as those of "the cranium of an unknown species" of Saurodontidæ. In his review of Dr. Crook's paper, Prof. Cope states that had it not been for certain conditions the figures of his species would have

been published, a statement which certainly implies that figures of it had not been published.

I have in my possession portions of several individuals that evidently belong to, or are very closely related to, Crook's species, and I am convinced that if Prof. Cope's figures, designated as belonging to his *Portheus arcuatus*, really pertain to it the latter and *Ichthyodectes polymicrodus* are very different. The parasphenoids of the two forms are different, as well as other bones, as Dr. Crook has observed. The latter held that Prof. Cope's figures belonged to *Ichthyodectes anaides*.

Having settled this, we return to the description of the type specimens of *Portheus arcuatus*, the maxillary and palatine. I quote Prof. Cope's language: "Apart from its small size, this species may be known by the compressed and concave alveolar border behind and below the posterior maxillary condyle and the very small size of the teeth which protrude from its subacute edge." It seems to me that this language and that which follows it (Cret. Vert., p. 204), as well as that employed in Proc. Amer. Philos. Soc., xvii, 177, agrees so well with the figure and description of Dr. Crook's species that no facts presented by him enable us to distinguish it from Prof. Cope's species. Nevertheless, it seems hardly safe as yet to unite the two. We ought to have more accurate descriptions of both. In looking over my specimens it seems to me that I can observe characters that indicate two species. In one maxilla I find that the posterior, or palatine, condyle is comparatively short and has in its hinder border a distinct notch; in other maxillæ the condyle is longer and apparently without the posterior notch. The distance between the condyles appears to be much greater in some cases than in others. There also appear to be some differences in the forms of the maxillæ.

While these forms can by no means belong to Cope's *Portheus* (*Xiphactinus* of Leidy), they can hardly belong to the genus *Ichthyodectes*. In the latter genus the maxilla is long, nearly equal to the distance from the tip of the vomer to the occipital condyle. The gape of the mouth must therefore have been large. In Dr. Crook's species and related forms, the maxilla is short, between one-half and two-thirds the distance referred to above; hence the gape of the mouth must have been rather small. The maxillæ of typical species of *Ichthyodectes* are nearly straight along the tooth-line, or sinuous, or, in *I. hamatus*, strongly concave. In *I. polymicrodus* the tooth-line is strongly convex, except just behind the palatine condyle. The teeth of *I. polymicrodus* are numerous and feeble: in the other species strong and in smaller number. Hence, for Prof. Cope's *I. arcuatus* and Dr. Crook's *I. polymicrodus* I propose the new generic name

GILLICUS.

Characters. A Saurocephalid with maxilla falciform, relatively short; teeth with roots, numerous, small. Gape of mouth smaller than in *Ichthyodectes*. Mandible deep. Base of skull with strong upward flexure. Scales large.

The genus is named in honor of Dr. Theodore Gill of the National Museum, who has also made additions to our knowledge of the fossil fishes. The generic name is formed in analogy with the word Aristophanicus.

As type of this genus I take Crook's *I. polymicrodus*, since it has been figured. Should this be shown to be the same as Cope's *I. arcuatus*, the latter name of course takes precedence.

Crook has interpreted the bones of the posterior upper region of the skull of his *I. polymicrodus* as he has those of *Portheus* (*Xiphactinus*); but, as in the case of the latter I am compelled to differ with him. However, many of the sutures are very difficult to demonstrate. According to Crook, the supraoccipital is greatly expanded in front, while the parietals lie laterad of the epiotics. It seems to me that the supposed expanded portion of the supraoccipital is really the area belonging to the parietals. There is a very distinct fold running along the hinder border of the expansion, and this, continuing up to the midline, has the appearance of a suture. In the crushed specimen before me, there is, along the middle line of the expansion, a break in the bone, but whether due to a fracture or to the parting of the bones along a suture, I cannot determine. Possibly the parietals were coössified along the midline. As to Crook's parietal, I cannot convince myself that there is any suture cutting off the area assigned to it from that assigned to the pterotic. I regard as pterotic the whole area extending from the posterior external angle of the skull to the lateral expansion considered by Crook as supraoccipital. See Crook's fig. 5, pl. xvi, Sq and Pa.

Crook's determinations of the proötic and the opisthotic are undoubtedly erroneous. His proötic is nothing but the lateral process of the parasphenoid which rises, on each side, to bound the eye-muscle canal. His opisthotic is the true proötic. It rises to the post-frontal, and assists in forming the articular surface for the hyomandibular, just as it does in *Xiphactinus* and our modern tarpon. The opisthotic is to be looked for further behind, and it seems to me that it occupies the whole or part of the area of Crook's figure 6, pl. xvi, which is designated by *Ocl.* There is in the side of the skull a deep excavation such as existed in the skull of *Xiphactinus* and exists in the skull of *Tarpon;* and the specimen in my hands and Dr. Crook's figure 6 give me the impression that, as in *Tarpon*

and probably *Xiphactinus*, the opisthotic sends forward a process below this excavation.

A remarkable feature of the head of this genus is found in the upward flexure of the forward part of the skull. At the anterior end of the basioccipital there is formed an angle of about 55° between the basal and the anterior parts of the skull. This reminds us of the figure of a young tarpon presented by Dr. Shufeldt in his work on Amia (Ann. Rep. Comm. Fish and Fisheries for 1883 (1885), pl. xiv). As regards *Tarpon* it is to be noted that in the adult fish this angle is greatly reduced, not exceeding perhaps 10°.

It seems rather remarkable that neither among Cope's specimens, nor those of Crook, nor those belonging to myself is there present an example of the premaxilla. Yet the surface of the maxilla indicates plainly that a premaxilla was applied to it, just as in *Xiphactinus* and *Ichthyodectes*. I do not see that it was relatively any smaller than in the two genera just mentioned, although it was doubtless much thinner.

While the skull in my possession is considerably crushed, and somewhat distorted, I am able to say with some confidence that the alisphenoids and orbitosphenoids were present and that they were quite as extensive bones as they were in *Xiphactinus;* but better specimens are needed in order to demonstrate their characters.

There seems to have been a nasal. As such I interpret a bone which is four or five times as long as wide, which lies mesiad of the nasal cavity and which articulates in front with the large ethmoid, while mesially it joins in part the ethmoid, but principally the outer border of the frontal.

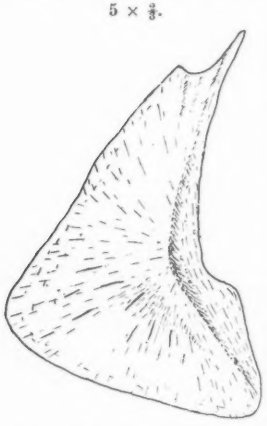
Crook has figured a portion of the lower jaw. The depth of this jaw in comparison with the maxilla is much greater than in the typical species of *Ichthyodectes*. The mandible appears to possess the same composition as that of *Xiphactinus*, viz., a dentary, an autarticulare and a dermarticulare, although it is possible that the two latter are consolidated. I am not able to find a distinct angulare. The cotylus for the quadrate is situated on the inside of a broad process, as in *Xiphactinus*. In my possession is the mandible of a large specimen of *Gillicus*, to the inner surface of which are appressed the hyoidean bones and the gill-arches. The hyoids and the gill-arches are so confused that not much can be determined regarding them. The hyoids were, however, very broad. A portion of a gill-arch displays an armature of small teeth. The gill-rakers were numerous, long, flat and wide, resembling those of *Tarpon*. Some of them are 48^{mm} long and, at the base, 5^{mm} wide. They were furnished with an armature of small teeth. The gill-rakers of the anterior arch were evidently more rigid than the

others. The hyomandibular seems to have had on its inner face a deep excavation, somewhat like that which I have described in the case of *Xiphactinus* (Zoolog. Bulletin, vol. i).

I have not enough of the vertebral column well preserved to enable me to determine its characters in this genus. It was doubtless much like the vertebral axis of *Ichthyodectes* and *Xiphactinus;* most of the vertebræ possess one or two deep grooves in each lateral surface. The upper arches were not coössified with the bodies of their vertebræ. Their bases occupied nearly the whole length of their centra; and evidently they came into contact in front and behind with the preceding and the succeeding arches. That there were anywhere in the vertebral column accessory pieces entering into the construction of the upper arches, such as I have described in *Xiphactinus*, I cannot affirm, but their presence seems probable.

On a block of soft limestone in my possession there occur a maxilla, a preopercle and several scales of an individual of this genus. The palatine condyle of the maxilla is relatively short, has a notch in its posterior end, and is separated from the anterior condyle by a space equal to two-thirds the length of the palatine condyle. A drawing of the preopercle, two-thirds the natural size, is here presented (fig. 5). The scales were relatively very large. Judging from the size of the maxilla, the fish could not have exceeded 60^{cm} (2 feet) in length. Nevertheless, one of the scales has a height of 44^{mm}. The imbedded portion of the scale is marked by grooves which radiate from the center of the scale and which are separated by spaces wider than themselves. The exposed portion of the scale appears to have been covered with numerous sharp points, which must have given a roughness to the whole body. These points were largest just behind the center of the scale. Toward the hinder edge they became smaller, and here the scale became striated with narrow grooves and ridges. It seems not unlikely that the free edge of the scale was pectinated, as in *Brevoortia.*

5 × ⅔.



U. S. National Museum, Washington, D. C.

ART. XXIV.—*On the Determination of Manganese as the Pyrophosphate;* by F. A. GOOCH and MARTHA AUSTIN.

[Contribution from the Kent Chemical Laboratory of Yale University—LXXIII.]

FOR the estimation of manganese in a gravimetric way when accuracy is a consideration, recourse is usually taken to the excellent method of Prof. Wolcott Gibbs.* This method consists in the precipitation of a manganous salt by an alkaline phosphate, the conversion of the tribasic phosphate into the ammonium manganese phosphate, and the weighing of the product of ignition as the pyrophosphate.

By Dr. Gibbs' original method the orthophosphate of manganese was precipitated by hydrogen disodium phosphate in large excess above the quantity required to cause the precipitation. The flocky white precipitate was dissolved either in sulphuric or hydrochloric acid, and precipitated again at the boiling temperature by ammonia in excess. This semi-gelatinous precipitate on boiling or long standing even in the cold becomes crystalline, the crystals forming beautiful talcose scales which have a pearly luster and a pale rose color. The precipitate was filtered off, washed with hot water, dried and ignited. The results obtained by Dr. Gibbs' students for the pyrophosphate accord closely with the theory.

Fresenius† showed subsequently that ammonium manganese phosphate dissolves in cold water, in hot water, and in an aqueous solution of ammonium chloride [1:70] to the extent of 1 part in 32,000, 1 part in 20,000, and 1 part in 18,000, respectively. It is clear, however, that the solubility of this precipitate is not indicated necessarily by the proportions given so long as an excess of the precipitant is present during the washing, though Fresenius did find in the filtrate traces of manganese which to his mind were sufficient to account for losses indicated by his test analyses, viz., one to three milligrams of oxide, or from two to six milligrams of phosphate.

Another mode of manipulation has been advocated by Blair‡ in order that the precipitate may be obtained more easily in crystalline condition. According to this method dilute ammonia is added drop by drop to the hot acid solution until the precipitate begins to form, the boiling and stirring are continued until the small amount of flocky precipitate is converted completely to crystalline condition, and the process of adding ammonia drop by drop is repeated until the manganese is all down in crystalline condition. The dilute ammonia is added in excess and the liquid filtered after cooling in ice water.

* This Journal, xliv, 216. † Zeitschrift für Anal. Chem., vi, 415.
‡ The Chemical Analysis of Iron, 106.

In discussing these methods of precipitation, McKenna* points out that both give good and accordant results, and that the process may be carried on in glass as well as in platinum, if the time of crystallization is made short enough.

When a manganous salt is precipitated in the cold by an excess of an alkaline phosphate, it falls, as Heintz† has shown, in the form of the trimanganous phosphate of the formula $Mn_3P_2O_8$. This same phosphate constitutes, as we have found, the greater part of the precipitate which forms when a manganous salt reacts in the cold in the presence of ammonium chloride with microcosmic salt and ammonia in slight excess. Boiling or even subsequent standing may, as is well known, effect a more or less complete conversion of the manganese phosphate to the ammonium manganese phosphate. Thus, in one experiment in which an amount of manganous chloride enough to produce 0·2214 grams of the pyrophosphate was precipitated in the cold by 5^{cm^3} of a saturated solution of microcosmic salt, with the subsequent addition of ammonia in excess, in a volume of 200^{cm^3} containing also 5 grams of ammonium chloride, the residue after ignition weighed 0·1904 grams. Presuming this residue to consist entirely of the pyrophosphate and the trimanganous orthophosphate, the proportion of the former to the latter calculated from the relation of symbols, and the weights taken and found, is nearly one to six. That is to say, about six-sevenths of the precipitate fell in this experiment in the form of the tribasic orthophosphate. In another experiment made exactly similarly, excepting that the liquid was heated to boiling, the proportion of the manganese pyrophosphate to the trimanganous orthophosphate in the only partially crystallized precipitate proved to be two to one. That is, in this case, two-thirds of the precipitate was in the form of the pyrophosphate. In the former of the experiments a small amount of manganese was found in the filtrate, but not enough to change materially the ratio recorded. The slight solubility appears to be connected with the incomplete conversion of the trimanganous phosphate to the ammonium manganese phosphate, for as will appear later, the manganese found in the filtrate, when the conversion is known to be nearly complete, is inappreciable unless extraordinary amounts of the ammonium salt are present. The success of the analytical process under discussion turns, therefore, upon the change of the trimanganous phosphate $Mn_3P_2O_8$ to the ammonium manganese phosphate NH_4MnPO_4. In the work to be described the attempt was made to learn the conditions under which this conversion may be best and most completely accomplished.

* Jour. Anal. Chem., v, 141. † Pogg. Ann., lxxiv, 449.

The conversion of a molecule of trimanganous phosphate to the ammonium manganese phosphate might be due, conceivably, either to the action of free ammonia or to the action of a salt of ammonium. The action of ammonia could only take place at the expense of a partial loss of manganese from the phosphate and its appearance as a hydroxide, two-thirds of the manganese going into two molecules of the ammonium manganese phosphate. In the presence of ammonium salts it is possible that the manganese oxide thus replaced might enter into union with the acid radical of the ammonium salt setting free ammonia; but if the ammonium salt present were the phosphate, or if an alkaline phosphate were present with other suitable ammonium salts, it is conceivable that the replaced manganese might appear as a constituent of a third molecule of ammonium manganese phosphate. In any event, it would be the ammonium salt and not the free ammonia which would determine the formation of the third molecule of the ammonium manganese phosphate. Plainly, too, the ammonium salt by itself, if it were a phosphate, or if a soluble phosphate were also present, might accomplish the conversion without the intermediate action of free ammonia. Unless, therefore, free ammonia favors the insolubility of the ammonium manganese phosphate, its presence would be unnecessary and might even be an actual disadvantage if the hydroxide naturally formed by its action upon the manganese phosphate were to fail to reunite fully with a phosphoric acid radical. It is plain, too, that the action of free ammonia might not stop with the replacement of one out of the three of the manganese atoms present in the molecule, but might even proceed under favorable conditions to the formation of phosphate richer in ammonium and to the separation of more manganese from its union with the acid radical. As a matter of fact Munroe* has shown that the prolonged action of hot ammonia upon the precipitate produced by the interaction of a manganous salt and an alkaline phosphate does actually produce a hydroxide which blackens as it takes oxygen from the air. Our attention has been given, therefore, more especially to a study of the conditions of action under which a salt of ammonium—the chloride—may bring about the conversion of the precipitate first thrown down by an alkaline phosphate to the form of the ammonium manganese phosphate. Experiments were made upon solutions of pure manganous chloride prepared and standardized by means of the sulphate method, as described in a former paper,† to show the effect of varying amounts of ammonium chloride on the condition of the precipitate and upon the solubility of the precipitate when

* Amer. Chemist, 1877. † This Jour. IV, v, 209.

once formed. The ammonium chloride for this work was prepared pure by boiling the chemically pure salt of commerce with a faint excess of ammonium hydrate and filtering—to free it from traces of iron, silica and alumina. In the first series of experiments dilute ammonia was added slowly to the hot faintly acidulated solution containing the manganous chloride and more than enough, theoretically, of a saturated solution of microcosmic salt to precipitate the manganese present. The liquid was heated and stirred until the flocky mass was changed to a crystalline condition. The addition of ammonia drop by drop, with constant stirring and heating, was continued until the manganese was all precipitated in crystalline form. A slight excess of ammonia was added and the liquid with the precipitate was allowed to stand for a half hour, cooling gradually or chilled in ice water. The precipitate was filtered off on asbestos under pressure, washed carefully in water made faintly ammoniacal, dried and ignited. The filtrates were tested for manganese by treatment with bromine and heating. The results of these experiments are given in the following table.

TABLE I.

$Mn_2P_2O_7$ equivalent to $MnCl_2$.		Error in terms of	Error in terms of	Saturated solution of		Manganese
Taken. grm.	Found. grm.	$Mn_2P_2O_7$. grm.	Manganese. grm.	$HNH_4NaPO_4.4H_2O$. cm^3.	Total vol. cm^3.	in filtrate.
0·4033	0·3769	0·0264 —	0·0102 —	5	60*	none
0·4033	0·3728	0·0305 —	0·0118 —	5	60*	"
0·3770	0·3530	0·0240 —	0·0090 —	5	60	"
0·3770	0·3620	0·0150 —	0·0058 —	5	60	"
0·4033	0·3751	0·0282 —	0·0109 —	10	60	"
0·4033	0·3774	0·0259 —	0·0100 —	10	60	"
0·4033	0·3871	0·0162 —	0·0062 —	5	200	"
0·3226	0·3066	0·0160 —	0·0062 —	5	200	"

* Chilled in ice-water.

In this method of precipitation of the manganese in a pure solution of a manganous salt the results are all wrong. The proportion of the trimanganous phosphate to the pyrophosphate in the residue, calculated from the symbols and the weights taken and found, is in the average two to five. That is to say, five-sevenths of the trimanganous phosphate has been converted to the form of the ammonium manganous phosphate.

The precipitate obtained in this manner is white and granular but not silky, and after ignition it shows the same dead white color, and is powdery. Evidently the regulation of the volume in which the precipitation is made is not essential, and the chilling of the liquid is of no importance in changing the

manganese to the ammonium manganese salt under the given conditions. It is plain, moreover, that the assumption of a crystalline condition can not serve as an indication that the composition of the salt is ideal. It is to be noted, however, that the conditions obtaining here are essentially different from those in common practice; for, ordinarily, when manganese is to be determined ammonium salts are abundantly present as the result of previous steps in analysis.

TABLE II.

$Mn_2P_2O_7$ equivalent to the $MnCl_2$.		Error in terms of $Mn_2P_2O_7$.	Error in terms of Manganese.	Saturated solution of $HNaNH_4PO_4 . 4H_2O$.	NH_4Cl.	Total vol.	Time of standing cold.	Manganese in the filtrate.
Taken. grm	Found. grm.	grm.	grm.	cm^3.	grm.	cm^3.	hrs.	
				A.				
0·1542	0·1520	0·0022 —	0·0008 —	5	5	200	15	none
0·1542	0·1540	0·0002 —	0·0000 —	5	10	200	15	"
0·1542	0·1536	0·0006 —	0·0002 —	5	10	100	5	"
0·1542	0·1535	0·0007 —	0·0002 —	5	20	200	2½	"
0·3770	0·3712	0·0058 —	0·0022 —	5	20	200	½	"
0·3770	0·3724	0·0046 —	0·0018 —	5	20	200	½	"
0·3084	0·3069	0·0015 —	0·0006 —	5	40	200	1	"
0·3084	0·3060	0·0024 —	0·0009 —	5	40	200	1	"
0·3084	0·3059	0·0025 —	0·0009 —	5	40	200	15	trace
0·3084	0·3057	0·0027 —	0·0010 —	5	60	200	15	none
				B.				
0·1542	0·1521	0·0021 —	0·0008 —	5	10	100	40	none
0·1542	0·1512	0·0030 —	0·0010 —	5	10	200	40	"
0·1542	0·1532	0·0010 —	0·0003 —	5	20	200	15	"
0·1542	0·1531	0·0011 —	0·0004 —	5	20	100	15	"
0·3770	0·3720	0·0050 —	0·0019 —	5	20	200	½	"
0·3770	0·3745	0·0035 —	0·0014 —	5	20	200	½	"
				C.				
0·1542	0·1519	0·0023 —	0·0009 —	5	15	200	..	none
0·1542	0·1530	0·0012 —	0·0004 —	5	20	200	..	"
0·1542	0·1525	0·0017 —	0·0007 —	5	30	200	..	"
0·3084	0·3020	0·0064 —	0·0025 —	5	10	200	..	"
0·3084	0·3053	0·0031 —	0·0012 —	5	20	200	..	"
0·3084	0·3033	0·0051 —	0·0020 —	5	20	200	..	"
0·3084	0·3039	0·0045 —	0·0017 —	5	60	200	..	trace

In the experiments of the next series the conditions are varied simply in this respect, that ammonium salts are introduced before the precipitation. The precipitate was less granular and more silky. After ignition the mass was white with a faint rose color. In the experiments of section A of the table the preci-

pitate first thrown down was redissolved, reprecipitated and filtered after cooling; in those of section B, the precipitate was filtered after cooling without resolution and without reprecipitation. and in those of section C, the first precipitate was filtered at once while the solution was still hot. The length of digestion before filtering and the indications of manganese in the filtrate are recorded in the table.

It was observed in these experiments that when the amount of ammonium chloride is present in considerable quantity a fine crystalline condition is got much more readily than when the amount of that salt is small: with maximum amounts of ammonium chloride the change from the flocky to the crystalline condition is almost immediate; even in the cold the change takes place to a marked extent in a few seconds. No manganese was found in the filtrate by boiling with bromine and ammonia—a test which is capable of indicating 0·0001 grams of manganous sulphate in 500$^{cm^3}$ of water containing 60 grams of ammonium chloride—until the ammonium chloride amounted to 20 per cent of the mass, or to 40 grams in 200$^{cm^3}$ of the liquid, and even then but once in three trials: even when the proportion was 30 per cent—60 grams in 200$^{cm^3}$—the solvent action of the ammonium chloride upon the manganese salt was trifling. The pyrophosphate residues obtained in these experiments, as well as in all those recorded in this paper, were dissolved in nitric acid and tested for contamination by a chloride; in no single case did silver nitrate produce more than an inappreciable opalesence in the solution. It is plain, therefore, that the variations of the results from theory are occasioned by variation in the degree of conversion of the trimanganese phosphate to the ammonium manganese phosphate, and that, while the ammonium chloride shows no appreciable solvent action on the precipitate in the presence of the precipitant, its effect in the process of conversion is plainly evident. For the smaller amounts of the manganese salts (equivalent to 0·1542 grams of the pyrophosphate) the effect of the ammonium chloride reaches a maximum when that salt amounts to 10 per cent of the solution; for twice that amount of manganese salt, the best results were obtained by doubling the amounts of ammonium chloride. Either line of treatment yields under the most favorable conditions, results which are passably good, but the advantage inclines slightly to the first method in which the first precipitate was dissolved and reprecipitated while the liquid was cooled before filtering.

In Table III are recorded results obtained by precipitating the cold acid solution of the manganese salt and the microcosmic salt with a strong excess of ammonia. The mixture was heated to boiling for from five to ten minutes and filtered hot.

In this series of determinations the amount of ammonium chloride present was constant while the volume of the liquid present was varied and the amounts of the microcosmic salt.

TABLE III.

$Mn_2P_2O_7$ equivalent to $MnCl_2$		Error in terms of $Mn_2P_2O_7$.	Error in terms of Manganese.	Saturated solution of $HNaNH_4PO_4.4H_2O$	NH_4Cl.	Total volume.	Manganese in the filtrate.
Taken. grm.	Found. grm.	grm.	grm.	cm^3.	grm.	cm^3.	
0·2214	0·2202	0·0012—	0·0005—	5	20	200	none
0·2214	0·2202	0·0012—	0·0005—	5	20	200	"
0·2214	0·2191	0·0023—	0·0009—	5	20	200	"
0·2214	0·2191	0·0023—	0·0009—	5	20	300	"
0·2214	0·2191	0·0023—	0·0009—	5	20	300	"
0·2214	0·2185	0·0029—	0·0011—	10	20	200	"
0·2214	0·2186	0·0028—	0·0010—	20	20	300	"
0·2214	0·2192	0·0022—	0·0009—	20	20	300	"

These results are possibly a trifle less satisfactory than those obtained for the smaller amounts of manganese by the method of Table II, it may be because the prolonged boiling tends to form a trifling amount of free oxide; but the fact is disclosed that an increase of the microcosmic salt is without influence and that a variation in volume from 200^{cm^3} to 300^{cm^3} is the occasion of little change in the indications of the process.

In another series of experiments the solution of manganous chloride was added drop by drop to the mixture of microcosmic salt and ammonium chloride made alkaline with ammonia. The precipitate which fell in the cold was crystallized by boiling the mixture a few minutes. The results are given below:

TABLE IV.

$Mn_2P_2O_7$ equivalent to $MnCl_2$.		Error.	Error in terms of Manganese.	Saturated solution of $HNaNH_4PO_4$.	NH_4Cl.	Total volume.	Manganese in filtrate.
Taken. grm.	Found. grm.	grm.	grm.	cm^3.	grm.	cm^3.	
0·1542	0·1521	0·0021—	0·0008—	5	5	200	none
0·2214	0·2203	0·0011—	0·0004—	5	10	275	"
0·2214	0·2192	0·0022—	0·0009—	5	15	275	"
0·2214	0·2197	0·0017—	0·0007—	5	20	275	"
0·2214	0·2223	0·0009+	0·0003+	5	20	200	"
0·1542	0·1528	0·0014—	0·0005—	5	30	275	"

The experience of this series of experiments demonstrated again that the ease with which the flocky precipitate is converted to the crystalline ammonium manganese phosphate is

proportioned to the ammonium chloride present, and the mean error of the results for the phosphate when the ammonium chloride reached 20 grams—0·0007 grm.—is considerably less than the mean error —0·0018 grm.—when the amount of the ammonium salt was less than 20 grms.

Experiments were also made according to the modifications suggested by Munroe,* viz., the boiling of the manganous salt with an excess of microcosmic salt until the precipitate becomes crystalline and just neutralizing with dilute ammonia; but we have been unable to find the conditions of this treatment by which uniform results may be obtained in even moderate agreement with the theory.

We have tried also the effect of substituting ammonium nitrate for ammonium chloride in the conversion process; but, so far as our experience goes, the nitrate is not so effective weight for weight in producing the change of the trimanganous phosphate to the ammonium manganese phosphates, while the solubility of the product in the solution of the ammonium nitrate becomes appreciable more rapidly with the increase of the amount present than is the case when the ammonium salt is the chloride.

In the light of the experiments described it would seem to be reasonable to expect the best results from the phosphate method for determining manganese when the conditions are so arranged that precipitation may take place in the cold solution in the presence of but little free ammonia, and of enough ammonium chloride to bring about the rapid conversion of the precipitate to the crystalline condition. Under such circumstances it should be possible to secure the conversion of the phosphate to the ideal constitution as completely as possible without danger of subsequent decomposition by the prolonged action of the hot free ammonia. In carrying out this idea, the solution of manganese chloride was treated as before with microcosmic salt and a large amount of ammonium chloride, the precipitate first formed was redissolved in hydrochloric acid and precipitation again brought about by the very careful addition of dilute ammonia in slight but distinct excess. The mixture was heated only until the precipitate became silky and crystalline, when it was allowed to stand and cool for a half hour. The precipitate was filtered off upon asbestos in a perforated platinum crucible under pressure, ignited and weighed. Table V comprises the results of experiments made in this manner. In those of section A the precipitation was made in platinum vessels; in those of section B the treatment was in glass.

* Loc. cit.

TABLE V.

A. In Platinum.

$Mn_2P_2O_7$ equivalent to MnO_2.		Error in terms of $Mn_2P_2O_7$.	Error in terms of Manganese.	Saturated solution of $HNaNH_4PO_4$.	NH_4Cl.	Total vol.	Manganese in the filtrate.
Taken. grm.	Found. grm.	grm.	grm.	cm^3.	grm.	cm^3.	
0·1885	0·1903	0·0018+	0·0007+	5	20	200	none
0·1885	0·1910	0·0025+	0·0010+	5	20	200	"
0·1885	0·1913	0·0028+	0·0011+	5	20	200	"
0·1885	0·1911	0·0026+	0·0010+	5	20	200	"
0·3770	0·3776	0·0006+	0·0002+	5	20	200	"
0·3770	0·3773	0·0003+	0·0001+	5	20	200	"
0·3770	0·3778	0·0008+	0·0003+	5	20	200	"
0·3770	0·3783	0·0013+	0·0005+	5	20	200	"
			B. In Glass.				
0·1885	0·1904	0·0019+	0·0007+	5	20	200	"
0·1885	0·1898	0·0013+	0·0005+	5	20	200	"
0·3770	0·3767	0·0003−	0·0001−	5	20	200	"
0·3770	0·3784	0·0014+	0·0005+	5	20	200	"

In this series of experiments the mean indication is, for the first time, in excess of the theory. Previously the error has been one of deficiency, and that in proportion to the amount of manganese handled, no doubt because the amount of unconverted trimanganese phosphate is proportioned to the entire amount of the phosphate. The positive error which is developed in this last series of determinations is probably due to the appearance of the natural error of all precipitation processes—viz., the tendency on the part of the precipitate to include matter in solution. In the previous experiments this effect was doubtless obscured by the incompleteness of the conversion of the trimanganous phosphate to the ammonium manganese phosphate. Indeed it is quite possible that even in the last determinations the conversion is not absolute, and that this is so suggested by the fact that the errors of excess are larger in the case of the smaller amounts of manganese for which the conversion throughout the entire work has appeared to be more complete. From the consideration of the results tabulated and described it would seem to be obvious that not only is the presence of ammonium chloride not objectionable in this analytical process, which depends upon obtaining the ammonium manganese phosphate from the trimanganese phosphate precipitated from a pure solution of manganese, but that its presence in not too small amount, or that of a substitute, is absolutely essential to make this conversion complete. For a given amount of manganese and a given volume of solution it

seems essential that the amount of ammonium chloride should reach a certain limit. According to our experience the proportion of ammonium chloride to the pyrophosphate should be at least 50 : 1; or, speaking approximately, more than 200 molecules of ammonium chloride must be present in the liquid (100^{cm^3} or 200^{cm^3}) to every molecule of the ammonium manganese phosphate to be formed. However, the quantity of the ammonium salt may be increased almost to the point of saturation of the liquid without causing more than a trifling solubility of the ammonium manganese phosphate in the presence of an excess of the precipitant. The statement of Fresenius and Munroe that ammonium manganese phosphate is soluble in ammonium chloride does not hold if there is an abundance of the soluble precipitating phosphate present. Further, our experience goes to show that the precipitate may be washed with perfect safety with pure water as well as with slightly ammoniacal water, or with ammoniacal water containing ammonium nitrate, if the filtration is performed rapidly and the precipitate is gathered in small space, as is the case when the phosphate is collected on asbestos in a perforated crucible. The finely granular precipitate which may be obtained by slow action of dilute ammonia added gradually to the hot solution of the manganese salt apparently includes a portion of unconverted phosphate which resists the replacement of the manganese by ammonium. On the other hand, the precipitate of flocky condition thrown down in the cold passes easily to the silky and crystalline condition when heated with the proper amount of ammonium salt and possesses a constitution approaching the ideal under such conditions. The conversion of the flocky manganous phosphate is so rapid that the precipitation may be carried on safely in glass vessels. If the ammonium chloride in the solution were to be included in the precipitate it would volatilize entirely during the ignition, leaving no trace unless, possibly, a portion of its chlorine were to combine with the manganese. Tests for chlorine in the residue of pyrophosphate resulted negatively—no more than a mere trace being found in any case, so that the contaminating effect of the ammonium chloride proves to be insignificant and the responsibility for the increase in weight above the theory must apparently rest with the included microcosmic salt.

In the practical determination of manganese by the phosphate method of Dr. Gibbs, therefore, we advocate strongly the presence of large amounts of ammonium chloride. Good results may be obtained by the method of precipitation originally laid down by Dr. Gibbs, or by the modification proposed by Blair, if the ammonium salt is present in sufficient quantity. On the whole trustworthy results are obtained most easily and

surely, according to our experience, by following the method of the experiments of Table V. The slightly acid solution, containing in a volume of 200$^{cm^3}$ (in platinum or glass) an amount of manganese not more than enough to make 0·4 grm. of the pyrophosphate, 20 grm. of ammonium chloride and 5 to 10$^{cm^3}$ of a cold saturated solution of microcosmic salt, is precipitated in the cold by the careful addition of dilute ammonia in only slight excess. The mixture is heated until the precipitate becomes silky and crystalline, the whole is allowed to stand and cool a half hour, the precipitate is collected upon asbestos in a perforated platinum crucible, washed (best with slightly ammoniacal water), dried at gentle heat and ignited as usual. By this process determinations of the larger amounts of manganese—0·4 grm. of the pyrophosphate—approximate rather more closely to the theoretical values than do those of the smaller amounts—0·15 grm. In either case the average error should not exceed 0·0010 grm. in terms of manganese.

Art. XXV.—*An Occurrence of Dunite in Western Massachusetts;** by G. C. Martin.

Introduction.—The occurrence of a mass of dunite in the Green Mountain region of Massachusetts is of interest and importance because it is a feature of the geology of that region which has apparently been hitherto overlooked, because there are on record only two other true dunites in North America, and because its mode of occurrence is such as to leave little doubt of its eruptive origin.

Location and Topography.—The rock occurs on the mountain south of Cheshire. This mountain is a spur of the Hoosac Range and although it is in the territory discussed by Wolff in his "Geology of Hoosac Mountain"† it is topographically distinct from the main mass of that range. This is shown on the contour maps, but is much more distinctly shown in the view from some of the neighboring peaks. The exact location of the dunite area may be found upon the Greylock sheet of the topographic map, or upon the geological map (Plate I) of Monograph XXIII U. S. Geol. Survey, by tracing the meridian 73° 10′ for 2¼ miles south from the village of Cheshire to its intersection with an unnamed stream. The area in question lies chiefly between this stream and Whipple Brook, the next to the southward. The main dunite mass occupies an area irregularly oval in outline and about 1000 by 2000 feet in extent. It is situated upon a flattened shoulder on the mountain-side, and is separated from the surrounding gneisses by brooks on the north and south, and by swamps on the east and west. Within the area are a number of rocky ridges 10 to 50 feet high, separated by swamps. About 400 feet northeast of the main mass is a smaller one of uncertain extent. (Loc. 351 as shown on the accompanying map.) Another exposure of doubtful relation to the main mass is east of the north end of it at Loc. 114 *c.*; while at numerous localities east and southeast of this, and northwest of the main mass at Loc. 304 the proximity of dunite is indicated by abundant fragments, some of which may be practically in place. In the banks of the Whipple Brook and at many places to the south, possible outcrops are to be seen, but since they may be merely glacial bowlders they are not mapped. Between all these and the main mass outcrops of gneiss intervene and no surface connection is visible.

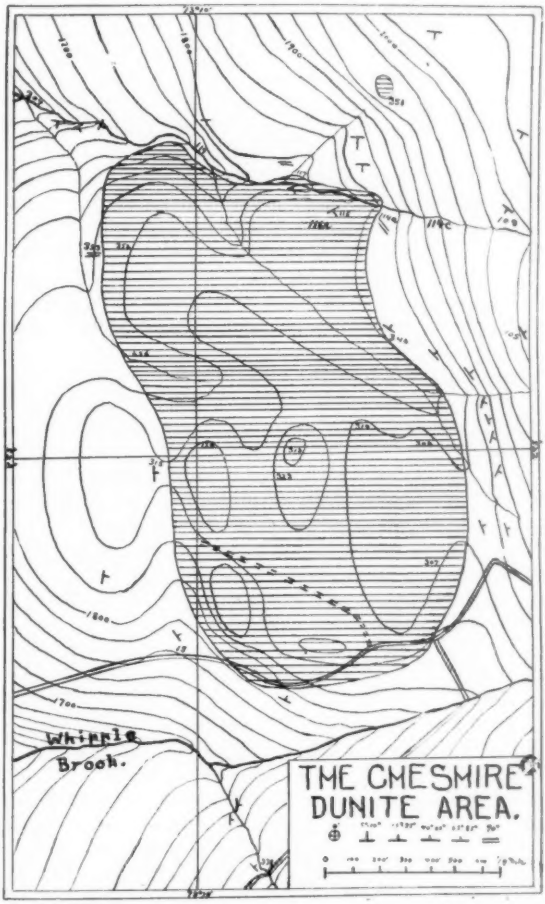
Description of Rocks.—The rocks of this area vary much in appearance; but as will be seen, the change from one form

* The author is indebted to Dr. A. C. Gill for advice and assistance in the preparation of this paper, especially in the chemical analysis, which is largely Dr. Gill's own work.

† Monograph XXIII, U. S. G. S., Part II.

to another is gradual and may be traced in the external appearance as well as in the mineralogical and structural details.

The most abundant and generally distributed form of the rock is hard, compact, and moderately fine-grained. In mass



the color is light to dark green, even approaching black, but the translucent splinters are light green usually with enough black specks to give the darker appearance. The density is from 2·9 to 3. The rock weathers readily in a well-marked zone to a yellowish brown "muscovado." This rock shows in thin section a badly shattered mass of olivine serpentinized along the cracks. Black opaque grains are scattered through it. The olivine fragments extinguish in groups, each of which

gives a uniform interference color. These groups are then the remains of former olivine crystals which are nearly uniform in size (·3 to 1^{mm}) and interlock to fill the entire field of the microscope. The cracks between the original olivines are no better developed than those between the shattered fragments. The serpentine is generally in fine cracks but often has recrystallized into needles varying in size from ·02 by ·1 to ·04 by ·5^{mm}. These in general follow the olivine cracks. But often there is a parallel arrangement of the serpentines and sometimes a tendency for all the serpentines of an individual olivine to arrange themselves in two directions nearly at right angles, —thus giving an appearance resembling Hussak's "gestrickte Structur," but showing by the enclosed olivine its derivation from that mineral instead of from pyroxene, as is usually assumed for that form of serpentine.

A specimen of this rock was powdered and the magnetic ingredients removed. Then by means of the Thoulet solution the serpentine was floated off. There then remained olivine with black grains scattered through it. The latter came down slightly in advance of the olivine and by repeated separations pure samples of each were obtained. The black non-magnetic grains had a brown streak and gave reactions showing the presence of iron, chromium, and aluminum. They are then doubtless at least partly picotite. The magnetic grains showed a trace of chromium. An examination of the olivine showed

Color ..... pale green
Sp. Gr. ..... 3·273 (not corrected for temperature, etc.)
Composition .

MgO	51·41
SiO_2	40·07
FeO	4·84
Al_2O_3	1·94
CaO	----
H_2O (ignition)	1·03
	99·29

The remaining rocks of the area range in density from 2·9 to 2·54. As the density decreases the macroscopic characters of the rock above described are gradually lost. The lightest rocks vary much from each other in texture and in color. Some are finely granular and homogeneous, some are schistose or shaly, and some are fibrous; some are black, light or dark green, yellow, white or mottled. But all grade, with the density, toward the type described above.

When these rocks are examined under the microscope it is found that the amount of olivine decreases with the density. And as the olivine decreases in amount, the serpentine increases by a gradual widening of the cracks. Recrystallization of the serpentine also takes place. Variation in rocks with the same

amount of serpentine depends in a large degree upon the amount of recrystallization and upon the relative positions assumed by these crystals. The magnetite is largely contemporaneous with the serpentine. It increases in amount with it, and shows a tendency to segregate into large grains, strings, and plates, some of several square inches in area and about ½ inch thick.

Other minerals are: hematite, with the magnetite; opal, occurring in cracks; chlorite, in irregular angular masses scattered throughout the dunite and serpentine; a carbonate, in the serpentine near the northeast corner of the main mass at Loc. 115; and a bronze non-magnetic mineral which gave the bead test for nickel and is probably niccolite, although with the quantities used no decided test for arsenic was obtained. The latter mineral is scattered in grains throughout the serpentine. The rocks of the area consist then of olivine and the serpentine which has been derived *solely* from its hydration. The original rock was a mass of olivine, with some members of the spinel group as minor constituents,—a strict *Dunite;* and it has hydrated in places to a *Dunite-serpentine.*

Field-Relations.—The olivine and serpentine are irregularly distributed, but the latter is in general more abundant around the border, especially at the northern end. Slickensides; a well marked foliation of the serpentine; and veins of fibrous serpentine traverse the area from north to south, dipping steeply to the east: but the foliation deviates from this general direction at the northern end, striking parallel to the border and dipping more moderately to the south. These characters are evidently due to shearing,—either that which accompanied the expansion during hydration, or that which attended some of the mountain-making movements by which the region has been affected. The slightly altered dunite which covers the greater part of the area has absolutely no structure but a strong irregular jointing.

The surrounding rocks are of a varied and complex character. The entire mountain was mapped by Wolff (Mono. XXIII, U. S. Geol. Survey) as "Vermont Formation (conglomerate, quartzite, and white gneiss)." The general structure is given as an overturned anticline with easterly dip and a strike varying somewhat from north. The presence of a dike of amphibolite is indicated in a position about half a mile north of the main mass of dunite.

The studies upon which this paper is based have shown that there are in the immediate vicinity of the dunite, beds of impure crystalline limestone, amphibolite, and gneiss. The limestone is apparently independent of the dunite, and it will be considered in a future detailed discussion of the entire mountain. The amphibolite is very generally distributed; is usually at least, interbedded with the gneiss; and the two are

extremely contorted. There is a general tendency toward a north and south strike with a steep easterly dip, but this varies extremely, as may be seen by the map. The dunite mass in its southern part is parallel to the strike of the gneiss, but at the northern end the bedding of the gneiss changes position, possibly forming a synclinal fold whose axis is cut by the dunite.

The contact of serpentine or dunite with gneiss is nowhere revealed. Outcrops of the two rocks are everywhere separated by eighty feet or more of swamp or by a drift-filled stream bed. In these places abound fragments of rotten gneiss and vesicular bowlders of gneiss, which latter are seldom elsewhere seen.

Structural Relations.—Concerning the structural relations of the dunite to the surrounding rocks, there are five hypotheses which may be considered.

1. That the dunite is a chemical deposit.
2. That it is a clastic.
3. That it is a bedded flow.
4. That it is a knob older than the gneisses and about which they were deposited.
5. That it is an intruded mass.

Of these the last seems best to accord with the following facts.

The unaltered dunite is uniform in character, has no trace of fragmental material, of recrystallization, or of bedding or banding of any kind.

There are an abundance of angular chloritic masses near the border, which on account of their aluminous character are probably the remains of feldspathic inclusions.

There are a number of outlying masses of dunite which can be connected with the main mass only as apophyses.

At several places the strike of the gneiss is directly toward the mass and in close proximity to it. (See map; east side, Loc. 346, 114*a*; west side, Loc. 353). These show conclusively that the dunite is discordant with the bedding of the gneiss.

The contact is deeply disintegrated and is marked by the presence of vesicular gneissoid bowlders, suggesting an alteration by an intruded mass.

Note.—In this connection it may be noted that there are in the Hoosac Range and to the east of it a considerable number of serpentine beds, many of which are not known to have been studied since the Hitchcock Survey and whose origin has not been made out. Some of them, however, are known to be derived from peridotites,* but these peridotites resemble all others in America, except those from Quebec, North Carolina, and the one here described, in containing, as original constituents, other ferro-magnesium silicates in addition to olivine.

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* Bulletin 126, U. S. Geol. Survey, pp. 10, 56, 152.

ART. XXVI.—*The Origin and Significance of Spines: A Study in Evolution;* by CHARLES EMERSON BEECHER.

[Continued from page 136.]

Summary of Causes of Spine Genesis.

Before taking up in more detail the various causes of spine development, and illustrating them by means of examples drawn from a number of classes of organisms, it is well to restate the factors which are believed to induce spine growth. This is especially desirable from the fact that, through the operation of unlike forces, similar conditions may produce the same morphological results, as in the differentiation of ornamental lamellæ and ridges, which, either from external stimuli or dispersion of growth force, may develop into spines. In such cases, it is difficult or impossible to distinguish the primary force, and the only satisfactory method is to discuss the subject under one head.

By carrying out this plan, and indicating the instances where the causes may replace or overlap each other, it may be shown how spines have originated, as follows:—

I. In response to stimuli from environment acting on most exposed parts. (A_1.)

II. As extreme results of progressive differentiation of previous structures. (A_2, B_2.)

III. Secondarily, as a means of protection and offense. (A_3, B_4, C_3, D_3.)

IV. Secondarily from sexual selection. (A_4, B_4, C_4, D_3.)

V. Secondarily from mimetic influences. (A_5, B_4, C_4, D_3.)

VI. Prolonged development under conditions favorable for multiplication. (B_1.)

VII. By repetition. (B_2.)

VIII. Restraint of environment causing suppression of structures. (C_1.)

IX. Mechanical restraint. (C_2.)

X. Disuse. (C_3, D_2.)

XI. Intrinsic suppression of structures and functions. (D_1.)

To illustrate the various causes of spine growth, representative examples which are believed to conform to the requirements will be selected from various groups of organisms. The number of spinose forms is so great that it will be impossible to give more than the briefest citation of a few of the leading types, especially those which have come under the notice of the writer; on this account the number of examples derived from the vegetable kingdom will be necessarily few.

I. *In response to stimuli from the environment acting on most exposed parts.* (A_1.)

The action of external stimuli falling on the most exposed parts of organisms is probably one of the most fundamental and fertile causes of spine production, since the relation between cause and effect is more direct and apparent here than by other modes of origin. In a general way, it comprehends all the remaining causes coming under the head of external stimuli, but for present purposes, it will be restricted by the elimination of secondary conditions, such as the indirect production of spines through differentiation of previous structures, and the action of external forces of selection.

The ruling forces in plants being so largely vegetative, or those of growth, and the cause of variation being principally physico-chemical and not molar, most of the modifications to produce spines will fall under other categories of origin (B, D) than the one now under discussion.

In the free swimming forms, however, as the Desmids and Diatoms, the external relations are found to be very much like those of animals. The frustrule of the Diatom, *Attheya decora*,[47] is quadrate in outline, and from the angles there extend sharp spinous processes, as represented in figure 32. The frustrule of the Desmid, *Staurastrum cuspidatum*, is composed of two triangular halves, and the spines project from the vertices of the angles. Other species of *Staurastrum*, *Xanthidium*, (*X. armatum*[47]), *Arthrodesmus* (*A. octocornis*[69]), etc., show similar spine growth from the most prominent portions of the frustrules. It is evident that in forms like these having angular outlines, any growth produced by external stimuli will naturally be greatest at the points of these angles, and in conformity with the previous analyses of these factors, a spiniform extension of the tissues would result.

Among the fresh-water Rhizopoda belonging to the Protoplasta (= *Amœbina*), the genus *Difflugia* affords good examples. *D. globulosa*[41] has a nearly spherical shell. In *D. pyriformis*,[41] the shell is elongate pear-shaped, and generally round on the summit or fundus, though in rare instances a central spiniform elevation is developed. This tendency becomes fixed in *D. acuminata*[41] in which the shell in general form resembles the preceding species, but the fundus is commonly prolonged into a single acuminate process (figure 33), though occasionally two or three spines are found. In *D. corona*,[41] there is a circlet of spines around the margin of the fundus besides the primary one in the center. *Difflugia constricta*[41] is a variable form, with the top of the shell generally smooth, though sometimes it is acuminate, and occasionally it has two or even a cluster of spines (figures 34–36). *Euglypha mucronata*[41] has a terminal spine, as in *Difflugia acuminata*.[41] *Placocista spinosa*[41] is a

flattened miter-shaped form with a distinct edge, along which are numerous spines. It should be noted that no spines are developed on any portion of these fresh-water Rhizopods except those here mentioned.

The Nasellarian Radiolaria furnish many instances of a terminal spine from the summit of the silicious helmet or cup-shaped skeleton, as in *Eucyrtidium elegans*,[24] *Podocyrtis Schomburgki*,[24] *Tridictyopus conicus*,[26] *Cornutella hexagona*,[26] etc. Many of the primary, or axial, spines in other sub-orders probably originated according to I. In the Spumellarian forms especially, the principal spines project from the prominent portions, as in *Trigonactura triacantha*,[26] *Hymenactura copernici*,[26] *Rhopalastrum triceros*,[26] *R. hexaceros*,[26] etc. The existence of similar non-spinose species shows that the formation of spines is independent of the growth of the normal prominences, as in *Rhopalastrum malleus*,[26] *R. hexagonum*,[26] etc.

In the Foraminifera, the configuration of certain forms is such that parts of the test are much more prominent than others, and in these exposed situations, the spines are most frequently developed. Some of the triangular Textulariæ have spines at the two lateral angles on the oral side. Some of the individuals of *Textularia folium*[9] show that similar spines were developed at different stages of growth, so that, in a full grown specimen, there may be two or three pairs of spines along the sides. Others, like *Verneuilina spinulosa*[9] and *Colivina pygmæa*,[9] develop spines from the points of each chamber. A number of species, also, show a single spine at the apex of the shell, as *Pleurostomella alternans*,[9] *Bolivina robusta*,[9] *Polymorphina sororia*, var. *cuspidata*,[9] etc. In the latter species, the ordinary form is rounded, or obtusely pointed at the fundus.

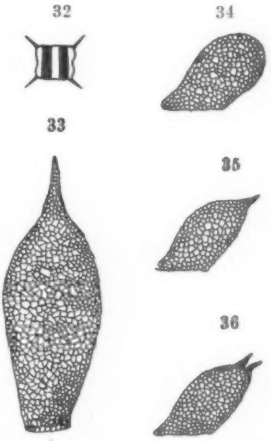

FIGURE 32. *Attheya decora*, a Diatom with spines from the angles. (From Mic Dict.)

FIGURE 33. *Difflugia acuminata*, a fresh-water Rhizopod, showing spiniform projection of the fundus. × 200. (After Leidy.)

FIGURE 34. *Difflugia constricta*, a fresh-water Rhizopod, with rounded fundus. × 175. (After Leidy.)

FIGURE 35. The same, showing a single spine on the fundus. × 175. (After Leidy.)

FIGURE 36. The same, showing two spines. × 175. (After Leidy.)

Some of the Infusoria have terminal spiniform processes, which, by analogy with other forms, have probably developed according to I, as *Ceratium tripos*,[9] *C. longicorne*,[9] *C. fusus*.[9]

The apertural spines on some of the Graptolites are on the most exposed portions of the hydrotheca, as in *Monograptus spinigerus*,[52] *Dicranograptus Nicholsoni*,[52] *Retiograptus tentaculatus* and *Graptolithus quadrimucronatus*. In many compound corals, the corallites are polygonal from crowding, and the most exposed portions, the angles of the calices, often bear spines, as *Favosites spinigerus*,[30] *Callopora exsul*,[30] etc. The spines on the septa and costæ of corals probably originate by intrinsic forces (B), since they are internal growths not influenced directly by external stimuli.

The spines on the ventral sacs of Crinoids are usually terminal, and in the most exposed situations; as in *Scytalocrinus validus*,[69] *Dorycrinus unicornis*,[69] *Aulocrinus Agassizi*,[69] etc.

The anterior and posterior pairs or rows of spines on the loricæ of some species of Rotatoria are in the most exposed places; as in *Anuræa squamula*, *Noteus quadricornis*, etc. The spinules on the tubes of *Spirorbis* are usually developed after it rises above the object of support so as to be exposed on all sides; as *Spirorbis spinuliferus*.[51]

The spinules at the corners of the angular cell apertures of many Bryozoa are in the most exposed situations, and probably arise through external stimuli; as in *Trematopora echinata*,[30] *T. spiculata*,[30] etc. The large marginal spines of the Brachiopod *Atrypa hystrix*[21] probably owe their excessive development to external stimuli, though the phylogeny of the species shows that the spines first originated through the differentiation of the radiate and concentric ornaments.

In many Pelecypods, the siphonal region receives a great amount of stimulus, and the post umbonal slope is the part most exposed. Along this slope are found many of the spines, and generally the greatest differentiation of ornament. Examples of spines on post-umbonal slopes may be seen in *Callista sublamellosa* and young *Saxicava arctica* (figure 27). Such spines represent periodic extensions of the mantle border, and in some cases, the stimulus for this growth may come from internal causes. The spines on *Unio spinosus* and related species are believed by Mr. Charles T. Simpson to assist in anchoring the shell in the sand of swift running streams. In *Callista*, the young *Saxicava*, and the Unios mentioned, the spines occur on all individuals and at such an early period as to preclude any special sexual function.

In the Gastropoda, the periodic extension of the shell over the posterior canal and the spiniform prominences formed on the labrum are situated in exposed places, or where the amount of stimulus is greatest; as in *Trophon magellanicus*, *Strombus pugilis*, *Fusus colus*, *Clavatula mitra*, *Melo diadema*, etc.

The spines on the larvæ of geometrid moths are usually on top of the loop, and are explained by Packard[54] as follows:

"The humps or horns arise from the most prominent portions of the body, at the point where the body is most exposed to external stimuli."

When the origin and function of spines in a great many forms of animals, and especially among the higher classes, are examined, it seems almost impossible to decide whether a spine has been originated and perpetuated by free variation and heredity, or by the general action of external stimuli on the most exposed parts; and in the latter case, whether or not under the selective influences of use. Its origin in either instance may be through external stimuli, but in the latter, it falls under other captions than A_1; or, in other words, the external stimuli excite the growth force at certain points, and the growths so produced may be simply reciprocal without function or they may serve purposes of protection or offense. Thus, the dorsal and rostral spines on the zoëa of the Decapods are on the most exposed points, and seem to function as defensive structures. As soon as the legs become well developed or when the animal ceases to swim at the surface and hides among the stones, etc., at the bottom, these spines become reduced and are often succeeded by others. The spines of the adult are also usually efficient for protection, but owing to the change in form of the animal and change of habitat, the most exposed parts are different from those of the larva, and the spines are frequently developed where there were no larval spines; as in *Cancer irroratus*, *Callinectes hastatus*, etc. Again, the horned ungulates show in their habits of sport, fighting, defense, and procuration of food, that the exposed angles of the top of the skull are subject to the greatest number of stimuli, and there the horns are developed. The connection between external stimuli and growth is here most manifest, for it is impossible to imagine the action of free variation or simple growth force as resulting independently, in the evolution of horned out of hornless species in several suborders of mammals, and in every case determining the location of the horns on the prominent angles of the skull, whether on the nasals, maxillaries, frontals, or parietals.

It is well known that toads and frogs defend themselves by using the head as a shield, and the cranial angles thus receive the greatest amount of stimulus. "There are natural series of genera measured by the degree of ossification of the superior cranial walls" (Cope[10]). In the highest genera, the head is completely encased, and in some forms the projecting angles are developed into short horns. The so-called "Horned Toad" (*Phrynosoma*) has the same habit of defense, and it is believed that this mode of protection or of receiving impacts has given rise to the structure, by stimulating growth at these points.

II. *As extreme results of progressive differentiation of previous structures.* (A_2, B_2.)

The differentiation of existing ornamental structures into spines has already been noticed in several instances in this article. It was shown that spines often arise by the elongation of nodes and tubercles or similar structures, by rhythmic alternating areas of growth in lamellæ and ridges, and by the growth of matter at the intersections of lines, lamellæ, ridges, etc. Furthermore, it was indicated that this progressive differentiation could be produced either (*a*) by the direct action of external stimuli affecting the amount of nutrition brought to a certain structure, (*b*) by the stimulus and dispersion of growth force, or (*c*) by a combination of the two forces. In this differentiation of the features which are generally called "ornamental," it will also be shown that the spine is the final result of progressive differentiation and, as previously indicated, can be formed out of a variety of other structures. The term "ornamental" is mainly one of human interpretation, and is used simply in apposition to "plain" or "simple"; for example, a clam cannot be imagined as consciously favoring a particular kind or arrangement of tubercles for ornamental purposes.

In a reticulate or cancellate surface formed by the crossing of raised lines, ridges, or lamellæ, it is evident that the causes or forces producing such structures will be increased at the points of intersection, and normally the amount of growth will here be greatest. In this way, it is possible to account for the very common presence of spines at the intersections of the radiating and concentric lines on many Mollusca and other organisms.

A few examples will now be given illustrating the differentiation of various structures into spines.

The points of intersections of the elements of the lattice in the Radiolaria are where spines are most frequently found; as in *Larnacalpes lentellipsis*, *Orosphæra Huxleyi*, *Carposphæra melitomma*, etc.[26] In *Xiphosphæra pallas*, the ridges about the openings or meshes are granular, and the intersections are raised into spines. Many of the discoid shells have their edges differentiated into spines, as *Heliodiscus asteriscus*, *H. cingillum*, *H. glyphodon*, *Sethastylus dentatus*, *Heliodrymus dendrocyclus*, etc. When an edge becomes elevated and defined as a carina, this structure is also often spiniferous, as in *Tripocalpis triserrata* and *Astropilium elegans*. The final differentiation of the radiate arrangement in the Radiolaria results in forms consisting only of a composite spine, as in the legion Acantharia.

In the Foraminifera, there are many instances of the gradual differentiation of carinæ, ribs, costæ, etc., into spines. In

Bulimina aculeata,[9] the surface nodes and granules become developed into spines. In *Textularia carinata*[9] and *Cristellaria calcar*,[9] the carinæ are spiniferous. The young of *Uvigerina aculeata*[9] is strongly costate, and later shell growth shows the costæ broken up into numerous spines. A related species (*U. asperula*[9]) has the whole test covered with spinules, which are sometimes arranged in lines, showing derivation from costæ. In *Truncatulina reticulata*,[9] the carina is made up of confluent spines, often discrete along the edge, and sometimes entirely separated.

37. 38. 39.

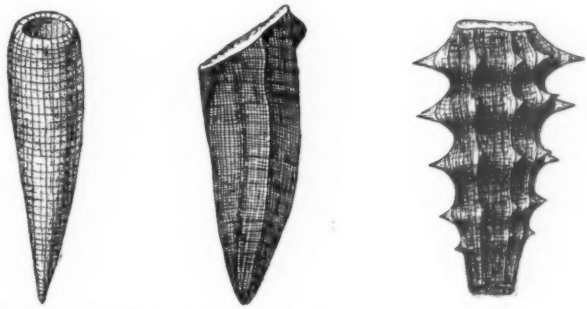

FIGURE 37.—*Cyathophycus reticulatus*. Ordovician. ½.
FIGURE 38.—*Dictyospongia Conradi*. Devonian. ½.
FIGURE 39.—*Hydroceras tuberosum*. Devonian. ½. (Figs. 37, 38, 39, after Hall.)
To illustrate progressive chronogenetic and ontogenetic differentiation in a family of hexactinellid sponges.

The hexactinellid sponges belonging to the family Dictyospongidæ show some very clear instances of the progressive differentiation of ornament in time and in ontogeny. The Ordovician *Cyathophycus reticulatus*[28] is a turbinate form, with a rectangular mesh of longitudinal and transverse spicular rays (figure 37). At more or less regular intervals, some of the spicules are larger, thus dividing the surface into larger rectangular areas. In *Dictyospongia prismatica*[28] from the Devonian, the domination of eight of the longitudinal bundles of spicules has produced a prismatic form. *D. Conradi*[28] is regularly an eight-sided pyramid or prism when young, but with the growth and elongation of the sponge, it developed slight undulations, then nodes, and later prominent tubercles (figure 38). *Ceratodictya annulata* and *Hydnoceras nodosum*[28] show a further specialization in the formation of rings and nodes. Practically the limit to these specializations is attained in *Hydnoceras tuberosum*[28] (figure 39), *H. phymatodes* and related forms. In *H. tuberosum*, the apex representing the young stage or the initial growth is much like *Cyathophycus*

or *Dictyospongia*. This is followed by a prismatic stage like *D. prismatica* and *D. Conradi*, then the nodes and tubercles are introduced and further growth produces the typical characters of the species. The tubercles are surmounted by a sharp spine formed at the intersection of two spicular laminæ, one concentric and one longitudinal.

Another type of surface specialization is shown in the genus *Physospongia* from the Keokuk group of the Lower Carboniferous. In this genus, there are bands of regular, alternating, elevated and depressed quadrules, the former frequently having the superficial layer of spicules extended into a spiniform process, as in *P. Dawsoni*.[28]

Among corals, there is occasionally some evidence of the external differentiation of structures into spines. The epitheca of the Tetracoralla frequently shows, by means of low lines or low ridges, the number and direction of the septa, and in some of the later species, these external septal lines are ornamented with rows of short spines or spinules; as in *Cyathaxonia cynodon*[18] and *Zaphrentis spinulosa*.[18]

Many Crinoids and Asteroids show the development of tubercles into spines, and the surface sculpture is often made up of ridges which bear strong spines at the points of intersection; as in *Gilbertsocrinus tuberosus*,[69] *Technocrinus spinulosus*,[69] *Actinocrinus lobatus*,[69] *A. pernodosus*, *Oreaster occidentalis*, *O. gigas*, *Retaster cribrosus*, etc.

The concentric laminæ of growth in the Brachiopods are frequently differentiated into spinules; as in *Siphonotreta unguiculata*,[31] *Schizambon typicalis*,[31] *Spirifer fimbriatus*,[31] *S. pseudolineatus*,[31] *S. setigerus*,[31] *Cliothyris Royssii*,[31] etc. Other species show the differentiation of the radii into spines; as *Acanthothyris spinosa*,[74] and *A. Doderleini*.[15] In others the strong concentric laminæ passing over radii are often infolded into spines; as in *Atrypa spinosa*.[31]

Among the Mollusca, innumerable examples could be cited showing clearly the differentiation of various ornamental features into spines. Some of these have already been discussed, but may be referred to again in this connection. Thus, an illustration of the passage of concentric laminæ into spines is shown in *Avicula sterna*[36] and *Anomia aculeata*[36] (figures 26 and 28), and *Margaritiphora fimbriata*, etc. Many species of Gastropods show the same types of differentiation. The differentiation of radiating lines or ridges into spines is equally common, and is well shown in *Spondylus* (figures 12, 14, 30), and in *Lima squamosus* (figure 40). In

40.

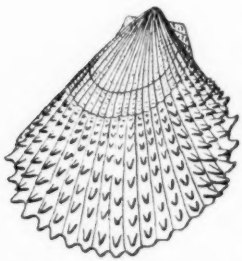

FIGURE 40. *Lima squamosus*. Natural size. To show differentiation of radii into spines.

most of these cases, the rib represents the progression of a fold in the edge of the mantle, while the spine is a process of a concentric lamina, and is usually more or less flat or tubular. Occasionally, the rib becomes obsolescent, and is represented by a row of spines, as in some specimens of the Gastropod, *Crucibulum spinosum*. When the radiating and concentric ornaments are distinctly continuous, a reticulate or cancellate appearance is produced, and the points of intersection often bear spines; as in *Aviculopecten scabridus*,[29] *A. ornatus*,[29] *Actinopteria Boydi*,[29] *Pterinopecten spondylus*,[29] etc.

The raised lines or ridges on the legs and carapaces of Crustacea are frequently spiniferous, as *Gelasimus princeps*, *Gecarcinus ruricola*, etc. The radii on the shells of barnacles are sometimes differentiated into spines; as in *Balanus tintinnabulum* var. *spinosus*.[13]

In the higher animals, the differentiation of ornamental features into spines is not common, especially as most of the forms are devoid of hard external parts. Among the fishes and reptiles, certain lines and ridges on the head and body are often spiniferous, while in others the scales have spiniferous ribs.

III. *Secondarily as a means of protection and offense.* (A_3, B_4)

After spines have originated through the stimuli from the environment acting on the most exposed parts, or by growth force, or by progressive differentiation of previous structures, they may often acquire added qualities, one of which is to protect an organism from the attacks of many of its enemies.

Morris[49] shows that defense in animals is either mechanical or motor, while in the higher plants, it is purely mechanical. The spine clearly belongs to the mechanical mode of defense, and in many animals may be efficient without motion. If motion is added, it then may serve not only for protection but for offense as well. Natural selection evidently could not originate a spine, but after one has appeared from any of the causes mentioned in the preceding paragraph, this agency could tend to preserve and allow the spine to develop along certain lines. The restrictions as a defensive structure would be those of efficiency, and therefore all the monstrous growths, vagaries, and ornamental spine features would arise independently of the action of protective selection, and would be accounted for by the operation of the forces of the environment, growth, and sexual selection. In this way, the simple antlers of the Tertiary Deer may be imagined to have reached the highest degree of efficiency as weapons, by ordinary natural selection (figure 41). In most cases, the subsequent increasing complexity of the antlers during more modern times cannot have improved their usefulness for protection or fighting

(figures 42, 43), and probably arose through gradual specialization according to the law of multiplication of effects, acted on by the agency of sexual selection. In some species, as the Reindeer (*Rangifer tarandus*), the differentiation of the antlers has secondarily produced a useful structure. One of the brow tines in this species has become greatly enlarged and palmated, and serves to assist in removing the snow to uncover food. Evidently this has had something to do with the common retention of the antlers in both sexes.

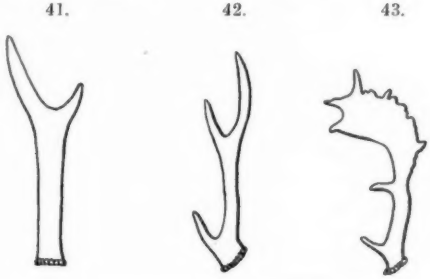

FIGURE 41. Antler of *Cervulus (?) dicranoceros*. Pliocene.
FIGURE 42. Antler of *Cervus pardinensis*. Pliocene.
FIGURE 43. Antler of the Fallow Deer (*Cervus dama*). Reduced. (After Nicholson and Lydekker.)

Certain types of horns are common to particular regions, especially when the cattle are in a semi-wild state, as in the Western Plains of America. The Texas cattle have long, gently curved horns standing out from the head. Similar forms are prevalent in the cattle of southern Italy and in other warm temperate regions. Farther north, the horns become more curved in a direction parallel with the head, and are therefore closer to the skull. The most northerly representative of the hollow-horned ruminants, the Musk-Ox (*Ovibos mochatus*) has the horns hanging down close to the skull and only curved outwards in their distal portions. Marsh suggests to the writer that these variations in the directions of the horns have been influenced by the climate. A warm climate permits the horns to stand out directly from the skull. Farther north, or in a colder region, the frequent freezing of the horns and their consequent drooping has induced a natural drooping condition, and an Arctic climate has resulted in the production of horns closely appressed to the skull, in which position they cannot be affected by freezing temperatures.

Another possible service for antlers is also suggested by Marsh. As is well known, the male Moose is one of the most wary of the Cervidæ, and detects noises at great distances.

The large palmate antlers act as sounding boards, and, when listening, the animal holds his ears in the focus of the anterior surfaces of the antlers.

The hollow-horned mammals afford some of the most evident examples of the use of horns for protection and offense. In species with permanent horns, like the bison, oxen, goats, cattle, antelopes, etc., the horns are generally present in both sexes, though in the males they are often much the larger. In defense, many of the horned ruminants hold the head down, thus protecting the nose and bringing the top of the skull into prominence. In this position, the horns are most effective. A similar posture is taken by the horned batrachians and lizards.

The Porcupine and Echidna rely largely on the protection afforded by their spines, and on this account they are sluggish in their movements, and make little effort to escape approaching enemies.

Many of the great horned Dinosaurs of the Mesozoic are well provided with an armature of protective plates and spines on various parts of the body. In addition to an armature on the body, *Triceratops*[46] had three large horns on the head, one median (nasal) and two lateral (supra-orbital). These were powerful offensive and defensive weapons. There were also other small nodes and spiniform ossicles around the posterior crest of the skull and on the jugals, forming a part of the general armor. In *Stegosaurus*,[42] the efficient offensive and defensive weapons were the huge spines on the tail, and it is interesting to note as a parallel to this condition, that the greatest nerve centers were in the sacrum, and therefore posterior also.

No group of vertebrates shows such a variety of protective and offensive characters as the fishes. Many of the older types were heavily plated, while in others the fin-spines were greatly developed. Among modern forms, the protective character of the spines is well shown in types like the Spiny Box-fish, *Chilomycterus geometricus* and *Diodon maculatus*. A combination of mechanical and optical protection is afforded in the remarkable Australian Pipe-fish, *Phyllopteryx eques*[25] (figure 49). This fish has numerous spines and ribbon-like branching filaments, the former giving it a mechanical defense, and the latter assisting in its concealment among sea-weeds, to which it bears a striking resemblance.

Spines for protection are extremely common among insects, even in larval forms. They have been so frequently noted as to require no elaboration here. Packard[44] has ably discussed the origin of nodes, tubercles, and spines, among certain caterpillars. Among the forms which feed exclusively at or near

the ground, he finds the body usually smooth, while those feeding on trees or on both trees and ground are often variously spined and tuberculated. These ornamental features arise from the modification of the piliferous warts common to all lepidopterous larvæ, and he concludes that the trees were more favorable for temperature, food, etc., than the ground, and that an increase of nutrition and growth force led to the hypertrophy of these warts into tubercles and spines. Having thus arisen, they immediately became useful for protection from birds and parasitic insects.

Among the Crustacea, there are also numerous examples of protective spines. These may be confined to parts of the body and legs especially exposed, or the entire animal may partake of the spiny character, as in the crab, *Echidnocerus setimanus*, where even the eye-stalks and antennæ are spiniferous. Others, like *Lithodes maia*, have the spines generally distributed over the carapace and legs. While serving for defensive purposes, this generally spinose character has probably reached its extreme development through the influence of repetition (B_2). The nauplius larva of *Lepas fascicularis* is very large, and has highly defensive spines which are explained by Balfour[3] as a secondary adaptation for protection. The larger spines on Trilobites, especially those from the genal angles and the axis, doubtless served protective purposes. The extremes of spinosity in this class are found in the various species and genera of the family Acidaspidæ, and also in many forms of *Arges*, *Terataspis*, *Hoplolichas*, etc.

Even among the star-fishes, which are so generally spinose, some forms have the spines so prominently developed on the most exposed portions of the animal that they evidently serve for protection; as *Acanthaster solaris*, *Echinaster spinosus*, etc.

The examples already given are sufficient to emphasize the fact that after spines are developed, they may then often serve for protection and offense and therefore be useful, their efficiency being controlled by natural selection resulting in the survival of the fittest.

Another process or kind of selection has been described by Verrill, as "Cannibalistic Selection." He has shown that the young of carnivorous animals often prey upon each other, as in the larval forms of some Decapoda, or sometimes even before the escape of the young from the egg capsules, as in some of the Gastropoda. Here, of course, any natural variation in the newly-hatched animals which would give an individual some advantage over its companions would tend to its preservation and to their destruction. In this way, it may occur that the relative growth of spines in the zoëa of decapods has

determined the survival of the well-armed individuals, as in the zoëa of *Cancer*[68] (figure 44), *Carcinus*, *Homarus*, etc.

44.

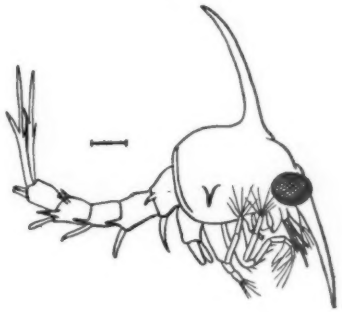

FIGURE 44. Zoëa of the common crab, *Cancer irroratus*; lateral view. ×8. (After Verrill and Smith[68].)

IV. *Secondarily from sexual selection.* (A_4, B_4.)

The males and females of so many animals present differences in size, color, and ornament, that corresponding variations in the development of spines, horns, and antlers, might naturally be expected. That such differences actually occur in nature is evident. Every gradation can be found between horns or antlers common to both sexes and those confined to one sex. Probably the initial difference is as ancient as sex itself.

Sexual variations of horns are most familiar among the mammals. Some, as the Giraffe, Ox, Bison, and Reindeer, have them present in both sexes, though the antlers of the female Reindeer are smaller and more slender than in the male, and in the American variety are sometimes absent. Others, as in the Prong-horn Antelope, many sheep, goats, etc., have the horns usually quite small in the female, and well developed in the male. Lastly, the modern Deer, Elk, Moose, etc., have the antlers confined to the males alone, the female being entirely without them.

Some of the early deer (*Procervulus*) seem to have had antlers in both sexes, and in nearly all the families of the Ruminata, there are species without horns, other species with horns in both sexes, and still others with horns only in the male. In the wild state, the presence or absence of horns and their character in any particular species seem to be well established, but in domesticated forms, the greatest variety is found. Among domesticated cattle, presumably of one species

originally, varieties are found without horns, and others with horns, showing all degrees of twisting and length.

By protecting cattle from enemies, by forcing them into changed environment, and by varying amounts of nutrition, man has evidently brought the original stock into a condition of free variation. This state has been made use of in the production of endless varieties by selection and cross-breeding.

Darwin[14] accounts for the sexual selection affecting the growth of the antlers in the Deer as due to excess in the number of male individuals, and their struggles for supremacy in the possession of a mate. The antlers at the breeding season are strong and solid, and are therefore at their maximum of efficiency in each individual. They are shed at or before the time the young are born. Previous to the growth and maturity of the new antlers, the young are so far advanced as to be able to avoid being killed by the adult males. Furthermore, Darwin suggests that the excessive development of antlers into palmate and arborescent forms was probably an ornamental character attractive to the females. These complicated antlers not being the most efficient weapons, the fighting proclivities of the males would tend to favor the individuals with simple antlers, and to repress the more differentiated forms. Thus, the two influences would be opposed to each other, though not necessarily equal. The law of the multiplication of effects may also have some force, since it may carry a structure beyond the bounds of efficiency. Even in one of the oldest horned mammals, the *Protoceras*[15] of the Miocene Tertiary, a great difference is seen in the horns of the two sexes. The female has little nodes or tubercles, which in the male rise to the height and prominence of the horns on the Giraffe, or are even relatively more pronounced.

The males of some other vertebrates have spiniform processes or spurs on their legs and wings serving particular functions. The spurs in birds are to be considered mainly as weapons which are used by the males in combats among themselves. They are developed on the metatarsal or metacarpal bones as bony processes ensheathed in horn. In the females, the spurs are generally rudimentary. A kind of spur is also found on the hind limbs of the male *Echidna* and *Ornithorhynchus*, attached to the astragalus. It is perforated by a duct leading from a gland. The functions of the spur and of the secretion are unknown.

Many lizards especially among the Chamæleons present striking differences between the sexes, and the males of some of them develop veritable horns like those in cattle, sheep, and other hollow-horned ruminants. Darwin[14] illustrates and describes a number of most interesting examples. One of

them (*Chamæleon Oweni*) is here shown (figures 45, 46). The male has three horns, one on the snout and two on the forehead. They are supported by bony excrescences from the skull. From the peaceable nature of these animals, Darwin concludes that "we are driven to infer that these almost monstrous deviations of structure serve as masculine ornaments."

The males of the tropical American genus of fishes, *Callichthys*, "have the spines on the pectoral fins stronger and longer than those of the female, the spine increasing in size as the male reaches maturity" (Seeley[65]).

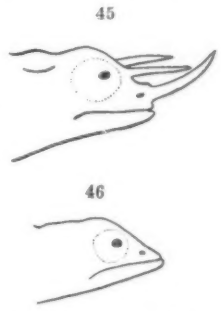

FIGURE 45. Profile of head of *Chamæleon Oweni*; male. $\frac{1}{4}$.

FIGURE 46. Female of the same species. $\frac{1}{3}$. (After Darwin.)

Among insects, the males of many beetles belonging to the Lamellicorns have long horns arising from various parts of the head and thorax. One of the best known forms is the Hercules beetle (*Dynastes hercules*). Bateson[5] states that, in this and other genera, it is commonly found that the males are not all alike, but some are of about the size of the females and have little or no development of horns, while others are more than twice the size of the females and have enormous horns. These two forms of male are called "low" and "high" males, respectively. Among the males, similar dimorphism in respect to size and length of horns occurs in *Xylotrupes gideon*, and in the stag beetle (*Lucanus cervus*, *L. titanus*, *L. dama*).

In many of these cases, the horns are evidently protective and not developed through the selective influences of the female. In such cases, the habits of the male are supposedly different from those of the female. Thus, Wallace[70] suggests that the horned males of the coleopterid families Copridæ and Dynastidæ fly about more, as is commonly the case with male insects, and that the horns are an efficient protection against insectivorous birds. These interpretations clearly do not come under the definition of sexual selection as restricted to the choice of either sex. Beauty, voice, or strength, may influence the selection of a mate by the opposite sex, but when the habits of the sexes are different and certain characters arise in response to this change, the explanation is then really found in the law of adaptation or physical selection.

V. *Secondarily from mimetic influences.* (A_5, B_5)

Natural selection may aid in furthering and preserving a spinose organism after the spines have originated through any primary cause. One aspect of this influence may be treated

under the head of mimicry. If, by their resemblance in form, color, or voice any characters are similar to characters present in the surroundings of the animal, and afford a means of protection or are useful, they may be considered as mimetic in the broadest sense of the term. Mimicry is usually restricted to a kind of special resemblance, and not to the cases of general resemblance afforded by an animal without significant colors in general harmony with its surroundings.

The influence of mimicry in the production of spines can only occur where the object mimicked is spiniform or spinose. Apparently this is rather infrequent and of little real importance as a factor of acanthogeny.

Insects and spiders have furnished the greatest number and variety of mimetic forms, both in their larval and adult conditions, and naturally would be expected to furnish examples of spines having mimetic significance. The object mimicked may be another species of insect or animal, in which case, there is usually some offensive or defensive quality rendering the resemblance useful to the mimicker; or, the whole or a portion of some plant or other object may be imitated, tending to the more or less complete concealment of the mimicking insect.

Satisfactory examples are not at hand, though doubtless many occur in nature, and some have been described, but not for the present purpose. A few will be cited here which seem to conform to the requirements.

47. 48.

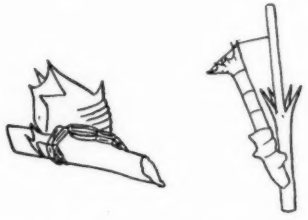

FIGURE 47.—Profile of a Spider (*Cœrostris mitralis*) on a twig mimicking a spiny excrescence. (From Peckham, after Vinson.)

FIGURE 48. The larva of the Early Thorn Moth (*Selenia illunaria*) resting on a twig; showing mimicry of stem and spiniform processes. ½. (After Poulton.)

A Madagascar spider (*Cœrostris mitralis*) is described by Elizabeth G. Peckham[56] as sitting motionless on a branch and resembling a woody excrescence with projections or spiniform processes, figure 47. Other spiny spiders of the Epeiridæ probably have similar protective mimetic features, as *Epeira spinea* and *Acrosoma arcuata.*

The larva of the Early Thorn Moth as described and illustrated by Poulton[58] bears a strong resemblance to the twig upon which it rests, even to spiniform processes, axils, and buds (figure 48). Packard[51] cites a striking case of mimicry in

49.

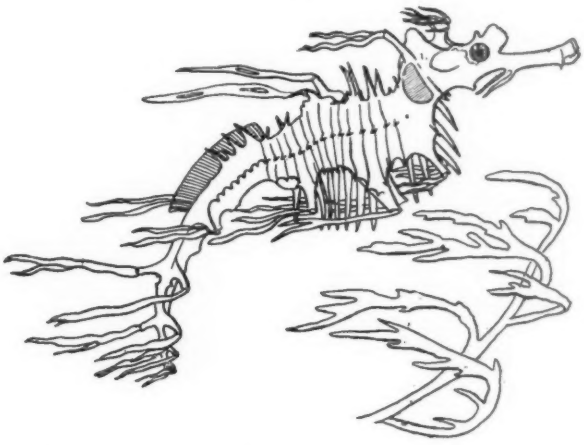

FIGURE 49. Australian Pipe-fish (*Phyllopteryx eques*) and frond of sea-weed in lower right hand corner; showing mimicry. ½. (After Günther.)

the caterpillar of another genus of moth (*Schizura*), where the spines and tubercles resemble the serrations of a leaf "so that when feeding on the edge of a leaf, the Schizuræ exactly imitate a portion of the fresh-green serrated edge of a leaf including a sere, brown, withered spot, the angular, serrate outline of the back corresponding to the serrate outline of the edge of the leaf."

The Australian Pipe-fish *Phyllopteryx*, previously mentioned under the head of spines for protection, shows the mimicry of a plant by an animal to a striking degree. This fish closely imitates a seaweed (figure 49) and Günther[25] gives the following description of the spines and filaments on the species *Phyllopteryx eques:* "There is a pair of small spines behind the middle of the upper edge of the snout, a pair of minute barbels at the chin, and a pair of long appendages in the middle of the lower part of the head. The forehead bears a broad, erect, somewhat four-sided crest, behind which there is a single shorter spine. A horizontal spine extends above each orbit. There is a cluster of spines on the occiput, and from these narrow appendages are prolonged. On the nape of the neck is a

long spine, dilated at the base into a crest, and carrying a long forked appendage. The back is arched, and on the under side are two deep indentations. The spines on the ridges of the shields are the strongest; they are compressed, are not flexible, and each terminates in a pair of short points. There is one pair of these spines in the middle of the back, and one on each of the three prominences of the abdominal outline; they terminate in flaps, which are long and forked. There are also very long compressed flexible spines without appendages, which extend in pairs along the uppermost part of the back, while a single series extends along the middle line of the belly. Small short conical spines run in a single series along the middle line of the sides, and along the lateral edges of the belly; and there is a pair of similar spines in front of the base of the pectoral fin. The tail, which is about as long as the body, carries the dorsal fin; it is quadrangular, and has sharp edges. It carries along its upper side five pairs of band-bearing spines, which terminate in branching filaments." *

The Horned Toad *Phrynosoma* bears considerable resemblance to the joints of the Prickly Pear, with which it is often associated, and it may be suggested that the likeness both in form and spinescence represents mimetic characters.

VI. *Prolonged development under conditions favorable for multiplication.* (B_1.)

The prolonged development or existence of a stock under favorable conditions for multiplication may be considered as one of the primary influences favoring the production of spines. This implies abundance of nutrition and comparatively few enemies outside of other individuals of the same or closely related species. Under a proper amount of increased nutrition, the vitality and reproductiveness of a stock are raised, and other things being favorable, it is found that the stock will give expression to what has already been described as free variation. Hypertrophy is also very apt to be one result of abundant nutrition, so that structures of little or no use may be developed, and some of them comprise certain features which are often called ornamental.

In the excessive multiplication of individuals, it is evident that there must be a great number of natural variations, and that some of these will affect the pairing of the sexes in such a manner as to accentuate and delimit certain variations. Eventually, there also comes a struggle for existence in which favorable modifications have a decided advantage. In this way, it

* The artist who copied Günther's figure for Lennis "Synopsis der Thierkunde," 3d ed., by H. Ludwig (vol. i. p. 770, 1883) connected the fish with the adjacent fronds of seaweed so as to form a single organism.

is believed that the great amount of differentiation found in some isolated stocks has been brought about. Primarily then, a favorable condition for nutrition is assumed, which is followed by excessive numerical multiplication; while the natural variations are augmented and governed by the action of reproductive divergence for which such conditions are favorable. Secondarily, these variations are subjected to the influences of cannibalistic selection, defense, offense, sexual selection, and mimicry.

In illustration of the amount of differentiation attained by a single stock under favorable conditions, the Amphipod Crustaceans, *Gammarus* and *Allorchestes*, found in lakes Baikal and Titicaca, respectively, may again be noticed.

In respect to the number of species, *Gammarus* is very sparsely distributed over the world, though in Lake Baikal alone a hundred and seventeen species have been described by Dybowsky.[17] In contrast to this, it may be mentioned that but four fresh-water species have been discovered in the whole of Norway. In Lake Baikal, all the depths explored (to 1373 meters) have furnished species. Those living near the surface are vividly colored, yet apparently make no attempts at concealment. Many of the species are also highly spinose, though not sufficiently armed to be protected from the fish. As these Crustaceans are voracious creatures, the spinose character has probably been favored by the agency of cannibalistic selection. The lake has a number of species of fish for which the Gammaridæ furnish excellent food, but the presence of a species of seal, predaceous fish, as well as the native fishermen keep the fish below the danger point, thus allowing the Gammaridæ to become very abundant.

Similarly, in Lake Titicaca, there is a wonderful specific development of a kindred Crustacean, *Allorchestes*. One of the most spinose species (*A. armatus*) is also the commonest, and according to Faxon[18] occurs in countless numbers (figure 50).

Packard[34] shows that, among certain moths, the caterpillars as soon as they acquired arboreal habits met with favorable conditions in respect to food, temperature, etc., and that as spines and tubercles arose by normal variation, such features being found useful for protection, were therefore preserved and augmented.

50.

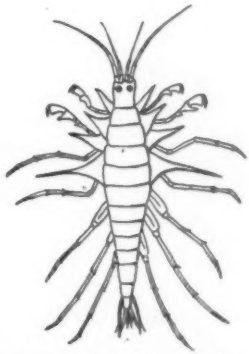

FIGURE 50. *Allorchestes armatus*. A spiny amphipod from Lake Titicaca. Female; dorsal view. Natural size = 9mm. (After Faxon.)

The differentiation of *Achatinella* has already been discussed (p. 132) as affording a striking instance of free variation among the Mollusca. The evolution of the Tertiary species of *Planorbis* at Steinheim, as described by Hyatt,[35] furnishes another example, though in neither case has the differentiation of structures proceeded far enough to result in spines. The costate form (*Planorbis costatus*) was tending toward that end, but did not attain it.

The series of Slavonian *Paludina* in the Lower Pliocene, as elucidated by Neumayr and Paul,[50] show a somewhat further advancement. The species in the lowest beds (typus *Paludina Neumayri*) are smooth and unornamented. Higher in the strata, they are angular and carinated, and at the top of the series, the shells are carinated, nodose, and subspinose (typus *Paludina Hœrnesi*). The living American genus *Tulotoma* is closely related to the most differentiated species (*P. Hœrnesi*), and its approach to spinose features is more pronounced.

Under the phylogeny of spinose forms (pp. 18, 19) an outline of the life history of the Brachiopod *Atrypa reticularis* and derived species was presented. This being one of the commonest types of Brachiopods in the Silurian and Devonian, often forming beds of considerable extent, it seems quite likely that its prolonged development under favorable conditions for multiplication must have had an effect on the amount and kind of variation.

It has been noticed by Brady[9] and others, that in the Foraminifera, *Globigerina bulloides*, *Orbulina universa*, etc., the pelagic forms comprise two varieties which are generally distinct, a spinous form and another with small minutely granular shells. The bottom specimens of the same species are also commonly without spines and often smaller. The interpretation seems to be that the large specimens indicate an abundance of nutrition which has also produced hypertrophy of the normal granules into spines. Some bottom specimens are large, but they are usually abnormal and of a monstrous or pathologic nature.

From the foregoing examples, the conclusion to be drawn is that, with full nutrition, there comes a numerical maximum, and naturally with this a corresponding number of normal variations. Some of these modifications, as spines, have arisen by hypertrophy. After having thus originated by growth force, they may or may not be of use for offense, defense, or concealment, or in any way give their possessor a distinct advantage.

[To be continued.]

SCIENTIFIC INTELLIGENCE.

I. Chemistry and Physics.

1. *A Laboratory Guide in Qualitative Chemical Analysis;* by H. L. Wells, M.A. 8vo, pp. viii, 190. New York, 1898 (John Wiley & Sons).—The purpose of the author in writing this book, as he tells us in the preface, was to introduce a method which, as he has found in his own teaching, has a "tendency to obviate thoughtless and mechanical work on the part of the student." The volume is divided into three parts. Part I comprises the Analytical Course, Part II the Theory and Part III the Descriptive Part; to which are added as appendices a list of apparatus and two sets of chemical labels. The object of the analytical course "is to introduce the subject of qualitative analysis in such a way as to develop the powers of observation, inductive reasoning and memory and at the same time to give a knowledge of chemical facts and methods which will be of use in the further study of this and related subjects." In general the methods of Fresenius are followed though with some changes. In the second part the student's knowledge of theory is supplemented by additional matter directly connected with analysis, the chapter on ions and ionization being especially valuable. In the third or descriptive part, the radicals are classified alphabetically, the properties upon which their analytical reactions are based being briefly given. The novelty as well as the excellence of the method developed in the Analytical Course seems of itself to justify the addition of this book to our analytical manuals. As a laboratory handbook it will prove most useful; being much smaller than the treatise of Fresenius, which must always remain the standard of reference. G. F. B.

2. *A Short Course in Inorganic Qualitative Analysis for Engineering Students;* by J. S. C. Wells, Ph.D. 12mo, pp. viii, 294. New York, 1898 (John Wiley & Sons).—This volume contains a short analytical course intended for the use of students who have only a limited time to devote to the subject. In the first section the grouping of the metals is considered, with the reactions of the several groups. In the second, the grouping and reactions of the acids are similarly treated. The third section is devoted to the analysis of actual compounds, especially of commercial products. The book is copiously supplied with "tables of scheme reactions," following the tables of group separations and those of separations of members of the groups. G. F. B.

3. *Introduction to Electro-chemical Experiments*; by Dr. Felix Oettel. Translated (with the author's sanction) by Edgar F. Smith. 12mo, pp. 144. Philadelphia, 1897. (P. Blakiston, Son & Co.)

Practical Exercises in Electrochemistry; by Dr. Felix Oettel. Translated (with the author's sanction) by Edgar F.

Smith. 12mo, pp. 92. Philadelphia, 1897. (P. Blakiston, Son & Co.)

The extensive introduction of electrical methods into chemical processes has given rise to the necessity of making electrochemical principles a part of higher education. In these little books Dr. Oettel has given in a complete form an outline of these principles and has thus done a service in this direction. The first volume is devoted rather to practical chemical electro-technics and the second to research methods. Dr. Smith's translation is an excellent one, as was to be expected from his well known position as an authority in this branch of chemical science. The books will do a good service in instruction. G. F. B.

4. *Remarks on Colloidal Glass;* by C. BARUS. (Communicated.)—Following the suggestions in my earlier experiments, given in this Journal (3), vol. xli, p. 110, 1891, I have since been enabled to impregnate glass with water to such an extent as to make it fusible below 200° C. The solution occurs with contraction of bulk relatively to the ingredients and increasing compressibility, substantially as already stated, (l. c.) Heated in a gas burner in air, the new clear glass melts, swells up enormously with loss of water to a white porous pumice resembling pith. Long boiling in water turns it white superficially.

I am now able to announce the following results: Glass as a colloid is miscible in all proportions with water.

If these solutions are sufficiently concentrated, they coagulate at ordinary temperature and the congealed aqueous glass is not different in general appearance from common glass. The melting point of the coagulated aqueous silicate frequently lies below 200° C., probably above 150° C., depending on the glass.

Brown University, Providence, R. I.

II. GEOLOGY AND MINERALOGY.

1. *Late Formations and Great Changes of Level in Jamaica;* by J. W. SPENCER. Abstract prepared by the author of a paper in the Transactions of the Canadian Institute, vol. v, pp. 324–357, 1898.—This paper is descriptive of the physical features of Jamaica which bear upon the evidence of great changes of level in late geological times, and extends the conclusions set forth in the author's work upon the "Reconstruction of the Antillean Continent."*

Speaking in a broad way, Jamaica is a dissected tableland, surmounting another but submarine plateau, extending from Haiti to the Yucatan banks, now submerged to depths of 3,000–4,000 feet. These banks have the form of old base-planes of erosion, but they are traversed by deep valleys more than 2,000 feet below the summit of the platform. Even within the limit of the submarine plateau mass, the channels reach to a depth of 9,600 feet, or more than 5,000 feet below the surface of the drowned plains.

*Bull. Geol. Sci. Am., vol. vii, pp. 103–140, 1894.

Here as everywhere, when studied, the valleys have in all respects the features of those of the plateau regions of Mexico and other countries. And they head in embayments of the land, receiving as tributaries the principal rivers of the district.

The modern topographic features of Jamaica date back, practically, only to the middle Miocene period; for the larger part of the island is covered by old Miocene white limestones. But the subsequent denudation has been enormous, for although the formation still reaches a thickness of 2,000 feet in some places, yet in others the dissection of it has penetrated the whole mass. Upon this old Miocene surface no Mio-Pliocene formations occur until those at the close of the period, showing it to have been one of long-continued elevation.

Upon these white limestones there was a subsequent mechanical deposit of marls, with pebbles (made up in part of older fragments), and in other localities there were gravels and loams (according to the source of the materials). These accumulations rise to a height of 500 feet in stratified beds, still nearly horizontal in contrast to the upturned beds of the underlying white limestone. They contain a few shells of modern species. The formations have been found to correspond, in position, with the Lafayette of the continent, or the Matanzas of Cuba, which have been provisionally placed at the close of the Pliocene period.

Overlying the Layton formation, where this has not been removed, and other formations found near the surface of the country, a mantle of stratified loams and gravels has been laid down. This occurs up to an elevation of 600 feet. It has been named the Liguanea formation, and has been correlated with the Columbia of the continent and the Zapata of Cuba. While no fossils have been found in this fragmental deposit, yet its stratified beds, occurring adjacent to the coast high above the sea, indicate its origin at sea-level. Thus it appears that the island was submerged to 500 or 600 feet during two distinct epochs, since the Mio-Pliocene period.

The paper describes the broad undulating features characterizing the Mio-Pliocene period. These have since been dissected by great deep valleys, extending from the land to the submerged plateau, formed subsequent to the Layton epoch; and from the depths to which they reach in the submerged plateau, the inference drawn is that the land stood 10,000 feet, or more, higher in the early Pleistocene period than to-day. The Layton formation, during this elevation, was enormously degraded, so that in many localities only remnants are found in protected places. Jamaica affords a favorable region for studying the contrast between the undulating topography developed near base-level of erosion during the Mio-Pliocene period of more extensive lands than to-day, and the great and enormously deep valleys of the post-Layton or early Pleistocene epoch. The molding of the submarine plateau is supposed to have occurred during the Mio-Pliocene period, while the deeply-drowned valleys are continuations of those of the land, which are of post-Layton age.

In contrast with these two features of erosion, that of the post-Liguanea epoch of submergence has been of small proportions; indeed, the post-Liguanea elevation is so recent that it has not passed beyond the stage of making narrow deep cañons. On account of this formation overlying the remains of the Layton series the different features of erosion, up to an altitude of 600 feet, are geologically preserved, while at greater altitudes they are not so easily distinguishable from those produced before the Liguanea epoch; yet when one has become familiar with the features of erosion, the respective epochs are generally recognizable. The post-Liguanea cañon-making epoch was characterized by an elevation of 150–200 feet more than at present; for the continuations of the existing rivers are traceable to that depth across the submerged coastal plains. The subsidence which caused the drowning of these valleys reached to an elevation of 10–25 feet below the present level; since which time the coral reefs of the coast have emerged to this amount.

Numerous as these oscillations appear, all of them, since the post-Layton elevations have been of comparatively small and diminishing proportions. These changes of level of land and sea have occurred on the other West India islands and on the continent; and from the amount of work accomplished, the Pleistocene period seems to have been one of long duration.

Outside of Jamaica, the geological features of that beautiful island would not be of special interest, except that here we find additional evidence, both upon land and the adjacent sea, supporting the theory of the high continental conditions of the West Indian region in the early Pleistocene period, when the land stood more than two miles above the present altitude, uniting North and South America, as is set forth in the "Reconstruction of the Antillean Continent."

2. *Resemblance between the Declivities of High Plateaus and those of Submarine Antillean Valleys;* by J. W. SPENCER. Tranactions of the Canadian Institute, vol. v, pp. 359–368, 1898.—This paper is a sequel to the "Reconstruction of the Antillean Continent,"* as in it the analysis of the slopes of the drowned valleys had not been considered. Both in the land and in the submarine valleys, their gradients are of two kinds: Those of rivers which are flowing over continental plains or upon the surface of high tablelands, where the declivities of the streams are so gentle as to be often reduced to even a foot per mile; (2) where the valleys are descending from higher to lower plateaus, in which case the descent is over a series of precipitous steps, separated by short gradation planes, marking pauses in the elevation of the land. Thus, if the mean descent of such a valley be taken, an average gradient would be entirely misleading. While the mean slope may reach from 100 to 200 feet per mile, it is found that in reality it is composed of perhaps twenty abrupt steps, with almost level flats between. Or the steps may reach a

* Bull. Geol. Soc. Am., vol. vii, pp. 103–140, 1894.

height of five hundred feet or more. Such features are seen descending from the Mexican plateaus (of 8,000 feet in altitude) to the Gulf of Mexico. The valleys end abruptly in amphitheaters indenting the floors of the tablelands and dissecting them.

In the drowned Antillean valleys, long reaches have been discovered with slopes of only a foot per mile, like that of the Mississippi, or of some plateau valley. These are separated by abrupt steps, similar to the succession of those descending from the margins of the Mexican tablelands. This point of analogy between drowned and land valleys, as well as the occurrence of short amphitheaters indenting the edges of the submarine plateaus, when carefully compared, very greatly strengthens the conclusions drawn in the "Reconstruction of the Antillean Continent"—namely that the valleys traversing the submarine Antillean plateaus were of land origin, and indicate the depth to which the West Indian continent has sunk, even to a depth of two miles or more.

3. *Die Eruptivgesteine des Kristianiagebietes*, Part III; *Das Ganggefolge des Laurdalits;* by W. C. Brögger. (Videnskab. Skrift. I Math. Natur. Klasse, 1897, No. 6, Kristiania, 8°, pp. 376.)—The already classic work, which Prof. Brögger has been conducting for many years, upon the igneous rocks of southern Norway, is well known to all petrological geologists. The appearance of the present important volume, giving as it does the results of much careful observation and study both in the field and in the laboratory, will be greeted with the greatest interest and attention by all who are interested in the many problems connected with igneous rocks. The special phase of the region which is handled in this memoir is the nephelite-syenite and the attendant varied and peculiar dike rocks which accompany it. Of the many subjects which are discussed it is only possible in this brief notice to summarize the more important.

There is given first a full description of the nephelite-syenite, which receives the varietal name of *laurdalite*. This is characterized by an unusual amount of lime and magnesia. It is accompanied by masses of *pulaskite*, a rather acid type, low in alkalies and poor in nephelite, and by mica-syenite. All of these are regarded as differentiation products of the normal augite-syenite (laurvikite) of the region.

The accompanying dike rocks are divided into two main classes: (*a*) the dark colored, generally basaltic types, rich in ferro-magnesian components (lamprophyres) for which the author proposes the name of *melanocratic* rocks (μέλας, dark and κρατεῖν to rule); and (*b*) the light colored types of which the feldspars are as a rule the chief minerals and of which the aplites are a representative class; for these the name of *leucocratic* rocks (λευκός white) is suggested. (It appears to the reviewer that these terms would have had a greater use and precision if they had been constructed as nouns instead of adjectives, since the terms they are proposed to replace are nouns, i. e. direct names of objects.)

The *melanocratic* rocks described are *camptonites, kersantites, vogesites* and *monchiquites* of various types; together with *minettes*, rich in soda and containing aegirite, and *farrisite.* Farrisite is a new type, consisting of barkevikite, colorless pyroxene, a little lepidomelane and traces of olivine, iron ore, apatite, etc., mixed with a colorless tabular tetragonal mineral of the scapolite group which plays the part of the feldspathoid and makes up about 35 per cent of the rock. The structure is fine-granular and megascopically the rock is deep chocolate-brown in color and very compact. Another new type belonging to this class is *heumite*, a dark-colored, compact fine-granular rock composed of barkevikite and biotite with alkali feldspars as chief components and with smaller amounts of nephelite, sodalite and diopside.

The *leucocratic* rocks are *nephelite-porphyry, tinguaite, sölvsbergite, bostonite, foyaite* (Brögger uses this term to designate normal nephelite-syenites with trachytic structure while those with hypidiomorphic granular structure he terms "ditroites") and *hedrumite.* The last-named rock type is defined as the chemical and mineralogical hypabyssal equivalent of pulaskite, possessing trachytic structure and therefore composed chiefly of alkali feldspar and poor in nephelite. In addition syenitic aplites are described under this group of alkaline type—the *lestiwarites* of Rosenbusch. Of all these types chemical analyses are given and the mineral composition and systematic position are thoroughly treated.

In the concluding portion of the work the bearing of the facts observed on theoretical petrology is discussed and it is shown that these dike magmas are to be regarded as derived from the laurdalite magma by differentiation, the melanocratic and leucocratic types being complementary derivatives. Many questions of general interest are handled including a masterly discussion of the "kern" hypothesis of Rosenbusch which it is shown can be only accepted in a modified form. The latter portion of the memoir is indeed full of suggestions and will furnish material for thought to all petrologists. L. V. P.

4. *Baddeckite, a new variety of Muscovite;* by G. C. Hoffmann. (Communicated.)—This interesting variety of muscovite was met with about half a mile from the town of Baddeck, Victoria County, in the province of Nova Scotia, where it occurs, in the form of minute isolated scales, small scaly aggregations, and thin scaly layers, distributed through a highly plastic clay; which also contains a large proportion of fine crystalline, white, pearly scales of kaolinite, some minute crystals of white quartz and small particles of pyrite and calcite.

The mineral has a fine copper-red color, a pearly luster, and affords a tile-red streak. With water it forms a highly plastic mass. Its specific gravity, at 15·5° C., is 3·252. Before the blow-pipe it fuses, at about 4·5, to a shiny black slag, which on continued heating in the reducing flame becomes magnetic. It

is decomposed by strong hydrochloric acid, with separation of slimy silica. An analysis by Mr. R. A. A. Johnston, upon very carefully prepared and apparently perfectly pure material, showed it to have the following composition :—

Silica	48·96
Alumina	13·85
Ferric oxide	25·82
Lime	1·17
Magnesia	2·65
Potash	3·47
Soda	0·22
Water (direct estimation)	3·78
	99·92

These figures afford a ratio for $RO : R_2O_3 : SiO_2 : H_2O$ closely corresponding to 1 : 3 : 8 : 2 giving the formula $H_4(Ca,Mg,K_2,Na_2)(Fe_2Al_2)_3Si_8O_{25}$, and assuming the hydrogen to be basic, the quantivalent ratio for $R' : R'' :$ Si of 3 : 9 : 16 or for bases to silicon of 3 : 4 agreeing with that required for some varieties of muscovite. The mineral is therefore a hydro-muscovite in which a very large proportion of the alumina ordinarily present is replaced by ferric oxide, and to this may be ascribed its exceptional behavior before the blow-pipe; its comportment with strong acids; as likewise its noticeably high specific gravity.

The name *Baddeckite* is given by the writer to this mineral from the above mentioned locality where it was first found.

5. *A Text Book of Mineralogy with an extended Treatise on Crystallography and Physical Mineralogy;* by Edward S. Dana. 593 pp. 8vo, with a colored plate. New York, 1898 (John Wiley & Sons).—A new edition of this work is announced as nearly ready; the following are quotations from the Preface:

"The remarkable advance in the science of Mineralogy, during the years that have elapsed since this text-book was first issued in 1877, has made it necessary, in the preparation of a new edition, to rewrite the whole as well as to add much new matter and many new illustrations.

The work being designed chiefly to meet the wants of class or private instruction, this object has at once determined the choice of topics discussed, the order and fullness of treatment and the method of presentation.

In the chapter on Crystallography, the different types of crystal forms are described under the now accepted thirty-two groups classed according to their symmetry. The names given to these groups are based, so far as possible, upon the characteristic form of each, and are intended also to suggest the terms formerly applied in accordance with the principles of hemihedrism. The order adopted is that which alone seems suited to the demands of the elementary student, the special and mathematically simple groups of the isometric system being described first. Especial

prominence is given to the 'normal group' under the successive systems, that is, to the group which is relatively of most common occurrence and which shows the highest degree of symmetry. The methods of Miller are followed as regards the indices of the different forms and the mathematical calculations.

In the chapters on Physical and Chemical Mineralogy, the plan of the former edition is retained of presenting somewhat fully the elementary principles of the science upon which the mineral characters depend; this is particularly true in the department of optics. The effort has been made to give the student the means of becoming practically familiar with all the modern methods of investigation now commonly applied. Especial attention is, therefore, given to the optical properties of crystals as revealed by the microscope. Further, frequent references are introduced to important papers on the different subjects discussed, in order to direct the student's attention to the original literature.

The descriptive part of the volume is essentially an abridgment of the sixth edition of Dana's System of Mineralogy, prepared by the author (1892). To this work (and future Appendices) the student is, therefore, referred for fuller descriptions of the crystallographic and optical properties of species, for analyses, lists of localities, etc., also for the authorities for data here quoted. In certain directions, however, the work has been expanded when the interests of the student have seemed to demand it; for example, in the statement of the characters of the various isomorphous groups.

6. *L'or dans la Nature;* by E. Cumenge and F. Robellaz. Premier Fascicule, 106 pp., Paris, 1898. (P. Vicq-Dunod et Cie, Éditeurs.)—This is a work of quite unusual character, in that it presents the subject of the occurrence of gold in nature in complete form from the various mineralogical, chemical, and geological standpoints. We have first a description of the crystallization of gold, then a summary of the composition of that from the different localities, and a general description of the occurrence of associated minerals. Following this is a brief chapter on the various minerals containing gold in nature and then an excellent digest of the gold regions in the different parts of the world. It is stated that the next *fascicule* will take up the subject of the distribution of gold in the geological formations, ancient and modern, auriferous gravels, and auriferous conglomerates, with a special study of the Transvaal. The work as thus far published can be highly commended, and in its complete form will doubtless prove of much value.

A series of thirteen excellent plates, which represent natural specimens of exceptional beauty of crystallization and interest of form, deserves very high praise.

III. Botany.

1. *The Illustrated Flora of the Northern States and Canada.** —When it was announced a few years ago that we were soon to have an illustrated flora of northeastern America, and that the preparation of this novel work was to be in the hands of Professor N. L. Britton, American botanists received the news with great interest. It was generally understood that on a number of fundamental points, such as the selection of both generic and specific names of plants and the conception of specific limits, the author of this proposed work was at variance with the usage of the distinguished botanist whose manual was then the only existing standard work covering northeastern America. It was, of course, assumed that in this new book those principles and conceptions would be worked out, and consequently, as the three volumes of the Illustrated Flora have appeared from time to time, they have been received with an interest doubtless greater than that which they would otherwise have aroused. Besides the desire to see the treatment of certain groups by Professor Britton and his associates, there has been a further anticipation of each volume on account of the illustrations—a unique feature in an American work of this scope. Altogether, then, this book must be regarded as one of the most important recent contributions to the literature of systematic botany.

The Illustrated Flora, as stated, has been prepared by Professor Britton, with the aid of a number of specialists and draughtsmen; and in the execution of the work the author has had the helpful coöperation of Judge Addison Brown. As we glance over the volumes, we are impressed with the neatness of their general appearance. The cuts, generally three on a page, are symmetrically arranged, dividing the space with the equally symmetrical descriptive text; and the accepted names, synonyms, descriptions, etc., have each their distinctive type.

In the adoption of the so-called Engler and Prantl system of arrangement, though as stated it is accepted with slight variations, the authors are to be congratulated, as that system, better than any other yet devised, gives us a near approximation to a natural arrangement of all plants. In capitalization, too, the book is certainly to be highly commended, for it adheres to good English usage, capitalizing the initial letters of all substantive specific names and all of personal or distinctly geographical origin. In fact, the work may be considered ultra-conservative on this point, adhering to the capital initial for geographical adjectives, a usage which many botanists, more conservative on the whole than the present authors, are tending to abandon. Another point which it is gratifying to see emphasized is the pronuncia-

* An Illustrated Flora of the Northern United States, Canada and the British Possessions; by Nathaniel Lord Britton, Ph.D. and Hon. Addison Brown. In three volumes. New York. 1896–98. (Charles Scribner's Sons.)

tion of personal specific names. In the Introduction it is recommended that such names be pronounced as nearly as possible as the men referred to would have pronounced them. In this way not only is a great deal of historic interest maintained, but there is the avoidance of many practically impossible Latin syllables.

The names adopted in this work are, as was expected, largely those of the so-called Botanical Club Check List, though in a number of cases other names, for some reason, have been substituted. This is not the place to discuss the nomenclature question—it would become too extensive a subject were one to take up its various phases. A recent paper* has shown very conclusively that the principles upon which the Check List is based are inconsistent, and consequently we can but regret that such names as will be only short-lived and which add confusion to the tangle of synonymy have been used in this work.

The English names, too, have received a great deal of attention, but unfortunately the authors seem to have lost sight of their true value and place. To many people it seems that if English names are to be given for the plants, they should be such as are actually used in colloquial speech by people who do not use the scientific appellations. Non-botanical people know only a comparatively limited number of plants—the commonest or most conspicuous or useful species—and for those they have their own names, sometimes imported from Europe, sometimes suggested by some characteristic of the plant, or often apparently a mere random name which has become fixed. Such names for a few species are numerous and often very different, and it is no simple matter to determine which are in most general use, but it is only such which should be used as colloquial names for plants. In a number of cases these standard names for showy plants are given, but in case of groups too inconspicuous or too difficult of separation for non-botanical folk to notice, the authors have manufactured a series of very uncolloquial designations—generally translations of the Latin names. Much time and thought must have been expended to accomplish what seems, unfortunately, a thankless task. Who that cannot say *Scleria reticularis* will ever say "Reticulated Nut-rush," or if he cannot say *Aster multiformis* will he be likely to speak of the "Various-leaved Aster"?

It is indeed a surprise in a work so ready to take up modern ideas to find the metric system of measurements quite ignored in the first volume. In the second volume, however, published after a number of adverse criticisms, the metric equivalents of the English units are given in a note, but the measurements are all given in the old standard feet, inches and lines.

It is not in these somewhat superficial matters alone, however, that a manual of systematic botany should be judged. Its worth as a working guide can be told only by use and by an examination of the descriptions, keys, ranges, specific limits, and, in this case, the illustrations. Reference has already been made to the neat-

*B. L. Robinson, Bot. Gaz., xxv, 437.

ness of the pages due in part to the studied symmetry of the descriptions; but this is secured at a very dear price, for through the carefully estimated symmetry of the text the most important point in scientific description, namely clearness, is lost. Most plants have not been over-described in the space allotted each species, but many trivial varieties (or, as generally treated here, species), which differ from the typical plants only in one or two details, could best be distinguished from those species by a mere phrase; while here that critical phrase is lost to the eye in a maze of unimportant details. For example, take *Houstonia ciliolata* and *longifolia* on page 214 of the third volume. These forms differ from each other only in minor and inconstant characters, yet an examination of the text will show that many general points in one description are repeated in the other, quite obscuring the essential differences which should be brought out. Again if the essential features of each species were in some way emphasized or contrasted with the distinguishing points of related species, much would be gained toward the clearness and ready usefulness of the work. In the Appendix this seems to be realized; but it would vastly increase the real value of the book as a field or herbarium companion if this method had been adopted before the last few pages of the third volume.

Intimately associated with the descriptions are the figures. These, as a whole are very attractive; but here, as in the descriptions, the test should not be the mere superficial appearance, but the presentation or omission of specific characters and the accuracy of details. From a general examination it would seem that in groups where the specific characters are largely habital the figures will prove of considerable service. In such groups, unfortunately, as require accuracy of detail and the representation of special parts, the figures are often most disappointing. A few groups should be made exceptions to this statement; for instance, in the *Naiadaceæ*, in which the text is by the late Doctor Morong and the figures are mainly reduced from the larger ones of his monograph, the details are very well brought out. In some groups, on the other hand, there seems not a little carelessness in either the drawings or the descriptions; at any rate, they are decidedly at variance. In the genus *Carex*, for example, it is surprising to find accompanying the description of *C. crinita* and the figure of a *crinita* perigynium a good habital sketch of *C. gynandra*. *Carex Raeana* is a slightly different case. Professor Britton reduces to *C. Raeana C. miliaris* var. (?) *aurea*, Bailey, a very different form; and he has figured as *C. Raeana* the latter plant. A comparison with Doctor Boott's plate of *C. Raeana* shows the Illustrated Flora figure to have striking differences. The leaves of *Salix Barclayi* are described as serrulate, yet in the figure the plant is represented with entire leaves. *Senecio sylvaticus* is distinguished from *S. vulgaris* principally by the simple involucre, lacking an outer short series; but the figure shows an involucre with the outer series of *S. vulgaris*. Other

careless drawings have been noted, but these cases are sufficient to show the caution which must be exercised in referring to the illustrations.

Another unfortunate feature of the drawings, not so much due to carelessness, is the omission of important details which must be relied upon, in many cases, for determination; or often the drawing of details in one case and their omission in contrasting cases. In Aster, for instance, very important characters are found in the involucre, yet hardly an involucre in the whole genus is drawn with sufficient accuracy of detail to be of much help. On the other hand, enlarged drawings are made in many cases of both ray and disk flowers, quite useless details without any readily accessible characters; and sometimes there is a drawing of a single involucral bract with no intimation whether it came from the outer, inner, or intermediate series.

In one group of *Aster* in particular, the section *Biotia* including the well-known *A. macrophyllus* and *A. corymbosus*, it was important that the illustrations, if any, should be perfectly accurate; for in treating this group alone Professor E. S. Burgess has described no fewer than ten new species and fourteen new varieties, besides reviving three old species. In view of the extended and most painstaking study which he has given this group, it was hoped that the presentation of his conclusions would make quite clear the diverse forms which constitute it. In this matter, however, we must confess great disappointment: from the descriptions alone, it is difficult to feel certain which of the new forms one has in hand. There are doubtless quite recognizable differences in the plants; but when the successful use of the key depends upon one's interpretation of the exact shade of difference between "predominant glands large, capitate" and "predominant glands minute, scarcely capitate," the student cannot help wishing for good enlarged figures of the glands. In two cases there are drawings presumably intended to show the glands, but, as no scale of measurement is given, it is impossible to compare even those with satisfaction. In attempting to make out these forms the student might make fair progress, after all, were he not hampered by the discrepancies between the descriptions and figures and even between the figures themselves. The second species of the group, *Aster tenebrosus*, is described as having "leaves very thin and smooth"; yet in the figure the leaves are represented as hairy as those of *A. Schreberi*, with "leaves . . . rough above, with scattered slender appressed bristles." The basal leaves of *A. curvescens* are said to have "a broad shallow sinus," and those of *A. nobilis* have "the sinus deep, broad, or the lobes overlapping"; yet in the figures it is difficult to detect a shade of difference in the sinuses. The basal leaves of *A. roscidus* are described with "the sinus deep," and the stem leaves are "chiefly orbicular and not cordate, with short broadly winged petioles, rarely slender-petioled"; but in spite of the description the accompanying figure shows an elliptic-ovate basal

leaf tapering gradually to the petiole, and similar but smaller sessile stem leaves. With such inconsistencies as these between descriptions and figures it is of course impossible to form any just opinion as to the validity of the species which are here described.

Throughout the work, as was expected, the tendency seems to be to regard as species many forms which have often been regarded merely as varieties. In many cases this course seems the proper one in view of recent studies and increased data. For instance, the separation of some forms from *Pyrola rotundifolia* seems quite proper: *P. asarifolia*, at any rate, is a plant with very different foliage and range, and its rose-colored flowers are expanded some weeks before those of the more southern white *P. rotundifolia*. *Amelanchier rotundifolia*, a species of northern river-banks, blooms in late May and in June, and matures its fruit in late August or September, long after that of *A. Canadensis* has fallen. It is a pleasure to see this plant put on the same basis as *A. Canadensis* and *A. oligocarpa;* but it is not quite clear how the Rochester Code allows the specific name *rotundifolia*, first applied as a varietal name to this plant in 1803, when there is already the European *A. rotundifolia*, Decaisne, founded upon *Cratægus rotundifolia*, Lam. Encyc., i, 84 (1783).

On the other hand, many of the old varieties, here raised to specific rank, seem to have less upon which to rest. The *Houstonias*, *H. ciliolata* and *H. longifolia*, already referred to, are well marked as extreme variations from *H. purpurea*, but with a large proportion of specimens falling between these different forms and showing many combinations of their characters, it is hard to see how they can be counted as of specific rank. In treating *Salsola*, Professor Britton keeps apart as species *S. Kali* and *S. Tragus*. How, after the observations of M. Constantin,* these plants can be regarded as more than forms of the same species, is not easy to understand. According to M. Constantin, when the seashore *Salsola Kali*, with coriaceous calyx and fleshy leaves, creeps up the rivers, the calyx becomes membranous and the leaves less fleshy, thus passing directly into the so-called *S. Tragus*. Contrasted with the treatment of *Salsola* the case of one of the common aquatics, *Myriophyllum humile* (*M. ambiguum*) may be taken. One form of the plant is very small with short leaves, and it grows in shores (*M. ambiguum*, var. *limosum*, Torr.). Another form, appearing very different, becomes even two feet long, has fine elongate-capillary leaves and grows in water (*M. ambiguum*, var. *capillaceum*, Torr. and Gray.) Yet Professor Britton (in this as in his general treatment of the group, closely following the late Doctor Morong) gives no recognition to these extreme forms, considering them "only conditions of the plant dependent upon its environment." What but environment, we may ask, has produced the peculiarities of *Salsola Tragus?*

* Jour. de Bot., 1887, 44.

In spite of the general tendency toward the elevation of minor forms to specific rank, there are a few noteworthy cases where well recognized forms have been reduced to other species. *Rosa lucida*, a species which with *R. humilis* has given eastern botanists more difficulty than almost any other common plant, is well treated, as formerly proposed by Mr. Best, as a variety of the latter species. In some other cases the reductions are less happily made. The case of *Carex miliaris*, var. (?) *aurea* has been cited. The related *C. miliaris*, var. *major*, Bailey, is unwisely reduced, it seems to us, to *C. miliaris*, Michx. The plants are in reality quite as different from one another as *Carex filiformis* and its variety *latifolia*, treated by Professor Britton as a distinct species, *C. lanuginosa*, Michx.

In discussing the specific limits and the figures in certain groups, mention has been made of the keys to species. These, of course, can be tested only by continuous use. Already the course of regular work has given an opportunity to try them in certain groups where carefully planned keys are important. In the genus *Aster* the key is based primarily upon the most obvious character of the plant,—the leaf—and, so far as it has been tested, with the exception of the group just discussed, it proves to be very helpful. In *Salix*, on the contrary, the key promises to be of little use, even to one somewhat familiar with the group. This is due to the illogical divisions, some of the primary groups being based exclusively on the staminate flowers, and their secondary divisions on the capsules.

The points already discussed, with the exception of accuracy of descriptions and figures, are matters to be decided in part by individual judgment; but there is one other essential to the good treatment of a flora, the geographical range of each species, in which absolute facts alone can be consulted. In determining the range of a given species it is possible to get an incomplete view by consulting a single large herbarium. A broader view may be gained by consulting a number of herbaria receiving large collections from different sources, and a still broader view is possible by consulting the more accurately prepared local floras. The most satisfactory results possible are gained by a combination of these methods, and it is asking none too much of our monographers to take advantage of all such opportunities as are open to them. Yet in the statement of geographic ranges the Illustrated Flora is exceedingly disappointing. The New England States, for example, have given issue to many lists and local floras, a number of them works of great accuracy, and the specimens upon which these publications are based are deposited in public herbaria or in private collections accessible upon request to critical students of systematic or geographic botany. In view of these standard publications and readily accessible herbaria, it is a surprise to find that in the statement of ranges of scores and scores of well known New England plants, their occurrence in the local lists is quite ignored.

Stellaria borealis (*Alsine borealis*, Britton) is one of the commonest plants in northern New England, extending northward to northern Labrador. The eastern range, as given in the Illustrated Flora, is "Rhode Island to northern New Jersey . . . . Ascends to 5000 ft. in New Hampshire."

Ranunculus multifidus is a common plant from central Maine southwestward throughout New England, yet the range given for that species (as *R. delphinifolius*) is "Ontario to Michigan, south to North Carolina and Missouri."

Nasturtium sylvestre (*Roripa sylvestris*, Bess.) grows near streams in Newfoundland and Maine (its occurrence in Maine reported in Bull. Torr. Bot. Club, xix, 340), but the range is stated "from Massachusetts to Virginia and Ohio."

Myriophyllum alterniflorum is a common plant in Maine waters and it extends to eastern Massachusetts. Its occurrence in Maine was published on the same page as the note on *M. Farwellii*, a species which Professor Britton has included from that State; yet in stating the range of *M. alterniflorum* no intimation is given that it grows in the United States.

Ligustrum vulgare is one of the commonest shrubs in rocky woods of eastern Massachusetts, recorded as a wild plant by Menasseh Cutler as early as 1785. The range here given is "Ontario and western New York to Pennsylvania and North Carolina."

Polygonum Careyi is locally abundant from northern Maine to Rhode Island, and its occurrence in Maine was given in Doctor Small's Monograph of the genus, and in his preliminary list (Bull. Torr. Bot. Club, xix, 353) Maine specimens are cited; yet now the same author gives the range "Ontario to Rhode Island, New Jersey and Pennsylvania."

But perhaps the strangest thing of all is to see our common *Lobelia spicata* entirely excluded from New England by the range "Ontario to the Northwest Territory, south to North Carolina," etc.

When we consider the multitude of species overlooked or ignored in a region so well represented by good local lists as is New England, it is easily seen what must be the experience of those who examine the Illustrated Flora with eyes familiar with plants of an area less thoroughly explored than that here taken as a standard.

In one other particular the Illustrated Flora is often disappointing. It aims to give in the synonymy of each species the recent current names of the plant. This is a good point and one which will be of great assistance to those who come face to face for the first time with the strange names here taken up; but if this detail could have been more carefully attended to, the usefulness of the book as a reference work would be enhanced. It is a disappointment in looking for some familiar name to find it absent, even as a synonym. One of our common elders has been known as *Sambucus racemosa*, but that name is not mentioned in the

treatment of the genus. An Arctic-alpine form of *Campanula rotundifolia* has been known to us as var. *Arctica*, yet that name is not given as a synonym of var. *Langsdorffiana*. A common *Luzula* in the White Mountains and northern Maine has been familiar as *L. spadicea*, var. *melanocarpa*, but under its more recent alias, *Juncoides parviflorum*, Coville, the more familiar synonym is not mentioned. In the so-called Botanical Club Check List the plant which we have known and which is now kept up as *Puccinellia maritima*, was called *Panicularia maritima ;* yet for some reason this name does not occur in the Illustrated Flora synonymy. One of the familiar White Mountain grasses has long passed as *Agrostis canina*, var. *alpina*, Oakes. In the Botanical Club Check List, Professor Scribner made a new combination, *Agrostis rubra*, L., var. *alpina*; but now in the Illustrated Flora the plant is called *Agrostis rubra*, and both the Check List name and the other are quite omitted from the synonymy.

In many particulars, then, the Illustrated Flora is hardly what we should like to see it. In most groups where the representation of minute details is important the figures can be used only with hesitation. The descriptions also, to one whose time is of value, are far from satisfactory. Printed in one style of type and often filled out with non-essential details, they are not readily interpreted. Unfortunately, too, the descriptions and the accompanying figures are often contradictory ; and in the statement of geographic ranges there has been so general an ignoring of well known and accessible data, that one can feel little confidence that the ranges of most species are given with even approximate accuracy.

On the other hand, there are fortunately some notable exceptions to the general run of figures. In the *Naiadaceæ*, *Alismaceæ*, *Gramineæ*, *Juncaceæ*, *Polygonaceæ*, and a few other families, most details are well brought out and the illustrations promise to be helpful. In the adoption of the Engler and Prantl system of arrangement too, the Illustrated Flora has taken a wise step ; and in spite of its inaccuracies and inconsistencies, when one wishes to gain from the Illustrated Flora only a general impression of the plant, it is certainly a great convenience. As a work for such reference it will find a welcome place in many libraries.

M. L. FERNALD.

Obituary.

Professor James Hall, State Geologist of New York from 1836 to 1898, died at Bethlehem, N. H., on August 7th, at the advanced age of eighty-seven years. A notice is deferred until another number.